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Vadose Zone Characterization and Monitoring

**Current Technologies, Applications,
and Future Developments**

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INTRODUCTION

NEEDS FOR VADOSE ZONE CHARACTERIZATION AND MONITORING

Vadose zone characterization and monitoring are essential for:

- Development of a complete and accurate assessment of the inventory, distribution, and movement of contaminants in unsaturated-saturated soils and rocks.
- Development of improved predictive methods for liquid flow and contaminant transport.
- Design of remediation systems (barrier systems, stabilization of buried wastes *in situ*, cover systems for waste isolation, *in situ* treatment barriers of dispersed contaminant plumes, bioreactive treatment methods of organic solvents in sediments and groundwater).
- Design of chemical treatment technologies to destroy or immobilize highly concentrated contaminant sources (metals, radionuclides, explosive residues, and solvents) accumulated in the subsurface.

Development of appropriate conceptual models of water flow and chemical transport in the vadose zone soil-rock formation is critical for developing adequate predictive modeling methods and designing cost-effective remediation techniques. These conceptual models of unsaturated heterogeneous soils must take into account the processes of preferential and fast water seepage and contaminant transport toward the underlying aquifer. Such processes are enhanced under episodic natural precipitation, snowmelt, and extreme chemistry of waste leaks from tanks, cribs, and other surface sources. However, until recently, the effects of episodic infiltration and preferential flow on a field scale have not been taken into account when predicting flow and transport and developing remediation procedures. The pronounced temporal and spatial structure of water seepage and contaminant transport, which is difficult to detect, poses unique and difficult problems for characterization, monitoring, modeling, engineering of containment, and remediation of contaminants. Lack of understanding in this area has led to severely erroneous predictions of contaminant transport and incorrect remediation actions.

For many years, it was assumed that wastes released or stored in the vadose zone would move slowly, if at all, through the vadose zone. Because of the emerging evidence of waste migration from leaking tanks through the vadose zone to the groundwater, scientists and engineers have begun to develop a strategy to investigate the vadose zone, including a comprehensive plan to assess vadose zone conditions.

OBJECTIVES

The overall objective of this chapter is to describe the current status, applications and future developments of vadose zone characterization and monitoring technologies using case-study data from practicing scientists and engineers. Using these data, we will recommend a series of site-characterization and monitoring methods, the development of both expedited and long-term vadose zone characterization and monitoring methods, and future developments for the design, performance, and post-closure of contaminated sites.

Because our understanding of a site is derived from field observations, this chapter describes the basic principles, advantages, and limitations of existing vadose zone characterization and monitoring methods,

using case studies from field experiences as well as the American Society for Testing and Materials (ASTM) and Environmental Protection Agency (EPA) standards related to vadose zone studies.

We will present evidence that the central problem of the vadose zone investigation is the preferential fast-flow phenomena and accelerated deep-contaminant transport toward the groundwater that has been observed at several sites. The methods discussed in this chapter can be used for the following purposes:

- Characterization of natural variations of flow and transport processes in vadose zone systems
- Characterization of anthropogenic stresses on vadose zone systems (such as induced point and non-point infiltration, and well injection)
- Design and selection of experimental methods for field and laboratory experiments
- Design of vadose zone remediation systems
- Project planning and data collection.

The methods and efforts required for conceptualization, characterization, and quantification of vadose zone systems for each application will vary with site conditions, objectives of the investigation, and investigator experience. We would like to note that this chapter is not intended to substitute for the thousands of excellent papers and a number of books on vadose zone problems (for example, Everett *et al.* 1984; Jury *et al.* 1991; Kutilek and Nielsen 1994; Wilson *et al.* 1995; Stephens 1996; Selker *et al.* 1999), but rather to present the main directions, advantages, and limitations of vadose zone characterization and monitoring methods.

CONCEPTUALIZATION OF VADOSE ZONE SYSTEMS

Conceptualization of vadose zone systems is needed for the integrated qualitative and quantitative characterization of unsaturated flow and transport processes affected by natural behavior and man-induced changes. Conceptualization is provided for any scale of investigation, including site-specific, subregional, and regional applications. Conceptualization involves a step-wise, iterative process of developing multiple

working hypotheses for flow and transport process characterization. These hypotheses are then used in selecting a proper combination of monitoring methods, interpretation, and analysis for refinement of flow and transport conceptual models.

A conceptual model is an interpretation or description of the physical system's characteristics and dynamics. The development of a conceptual model is an important step for site characterization because an incorrect model can lead to significant errors in the development of mathematical and numerical models, thus adversely affecting predictions and planning of remediation efforts. The development of a conceptual model is based on the analysis and simplification of data collected during field-monitoring and laboratory experiments, simplification of hydrologic systems, and the representation of hydrogeologic parameters in models (Boulding 1995). In general, conceptual models that describe water flow include a description of the hydrologic components of the system and how mass is transferred between these components.

Without a conceptual model, we do not know what tests to conduct, what parameters to measure, where to place probes, or what probes to use. Conversely, without such data, we cannot develop a conceptual model. This situation requires an iterative approach, in which we conduct a series of observations and tests and, concurrently, develop a conceptual model of water flow to refine our tests. The development of a conceptual model for water flow in the heterogeneous soil and fractured rock of the vadose zone is particularly difficult for three main reasons:

- (1) The contrasts in permeability of soils and rocks at different parts of the system may be extreme and localized.
- (2) The geometry of water flow depends strongly on the interconnection or connectivity of a preferential-flow-zone network. In a given vadose zone system, many probes may be located within nonconductive zones, which have no significant role in flow. In fractured rocks, fractures may be nonconductive because apertures are closed under the ambient stress state or by mineral precipitation. Additionally, soil and rock hydraulic conductivity may decrease during an infiltration event because of clogging, sealing, or air entrapment.
- (3) The design of borehole tests and the interpretation of data in heterogeneous soils and fractured rocks are complicated because the

response in a monitoring well may only be from a single zone of preferential flow or a fracture (Long 1996). Therefore, “point” measurements in heterogeneous soils and fractured rocks cannot reveal complex processes that result from the interaction of features at many different scales.

Conceptualization begins with a theoretical understanding of the entire groundwater-vadose zone-atmosphere system, followed by data collection and the refinement of that understanding. Additional data collection and analysis, as well as the refinement of the groundwater system conceptual model, occur during the entire process of conceptualization and characterization, and during groundwater model development and use (Figure 3-1).

Numerical modeling (forward and inverse) as a means of developing a flow-and-transport-process conceptual model allows us to obtain a better understanding of the level of detail and features needed to improve site-characterization design and monitoring methods.

WATER FLOW AND CHEMICAL TRANSPORT PROCESSES IN DEEP AND SHALLOW VADOSE ZONES

SPATIAL AND TEMPORAL SCALES OF VADOSE ZONE INVESTIGATIONS AND SCALING

Spatial Scales

Heterogeneity of hydraulic processes in soils and sediments occurs in a hierarchy of spatial and temporal scales (Cushman 1986; Faybishenko 1986; Wagenet *et al.* 1994; Wheatcraft and Cushman 1991). Heterogeneity of soils and sediments on different scales and nonuniform areal precipitation and run-off are the main causes of the multiscale flow phenomenon in the vadose zone. The conventional soil-science approach considers flow processes to occur on several scales, shown schematically in Figure 3-2.

This figure illustrates pore (microscopic), Darcian (mesoscopic), and catchment (megascopic) scales. The basic element of soil used for field studies is called a pedon. The pedon is a three-dimensional body having a land surface area of 1 to 10 m². The “pedon-scale” investigations are then used to extend the results to a large field scale. Kutilek and Nielsen (1994) proposed the inclusion of two categories within the catchment

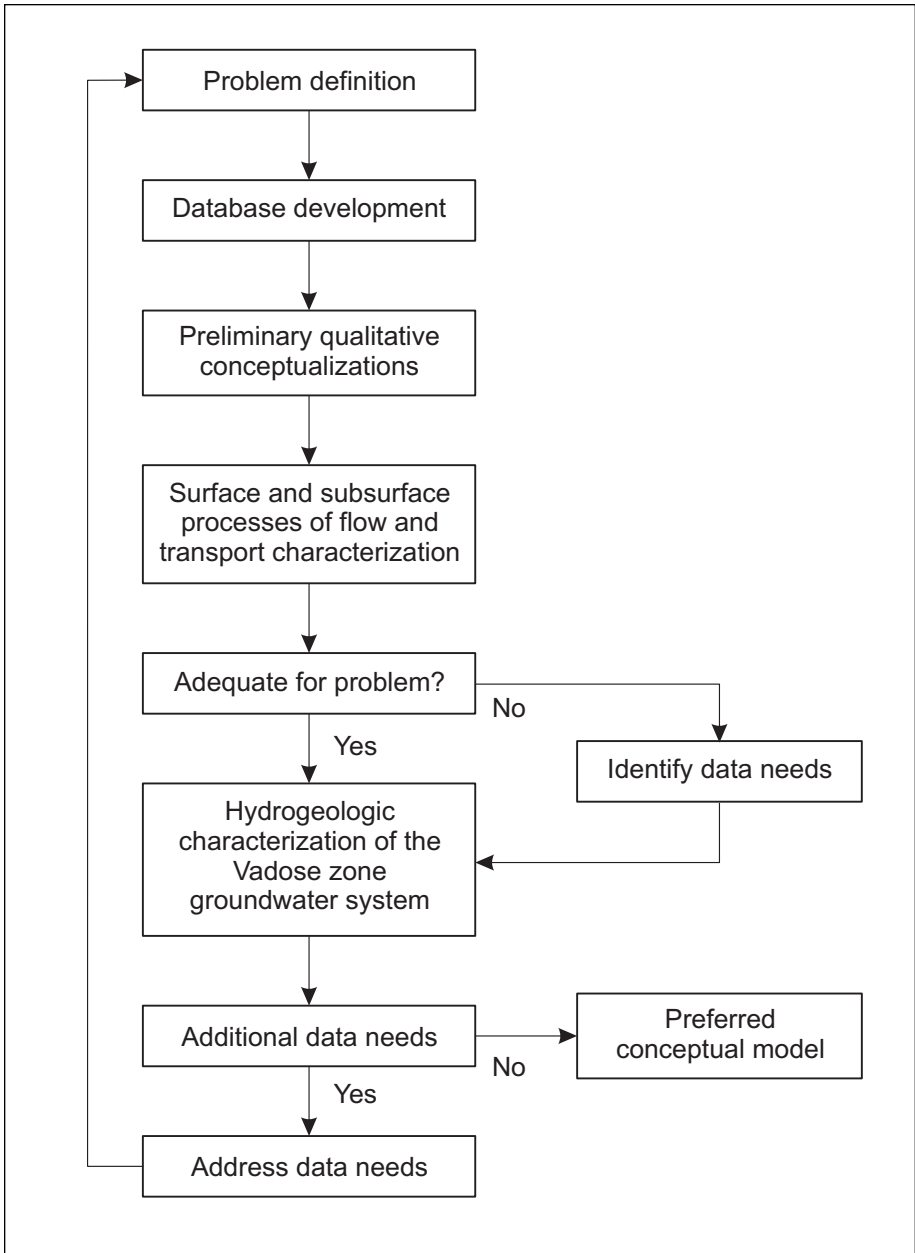


Figure 3-1. Procedure for Conceptualization and Characterization of Vadose Zone - Groundwater Flow Systems (modified from Kolm *et al.*, 1996)

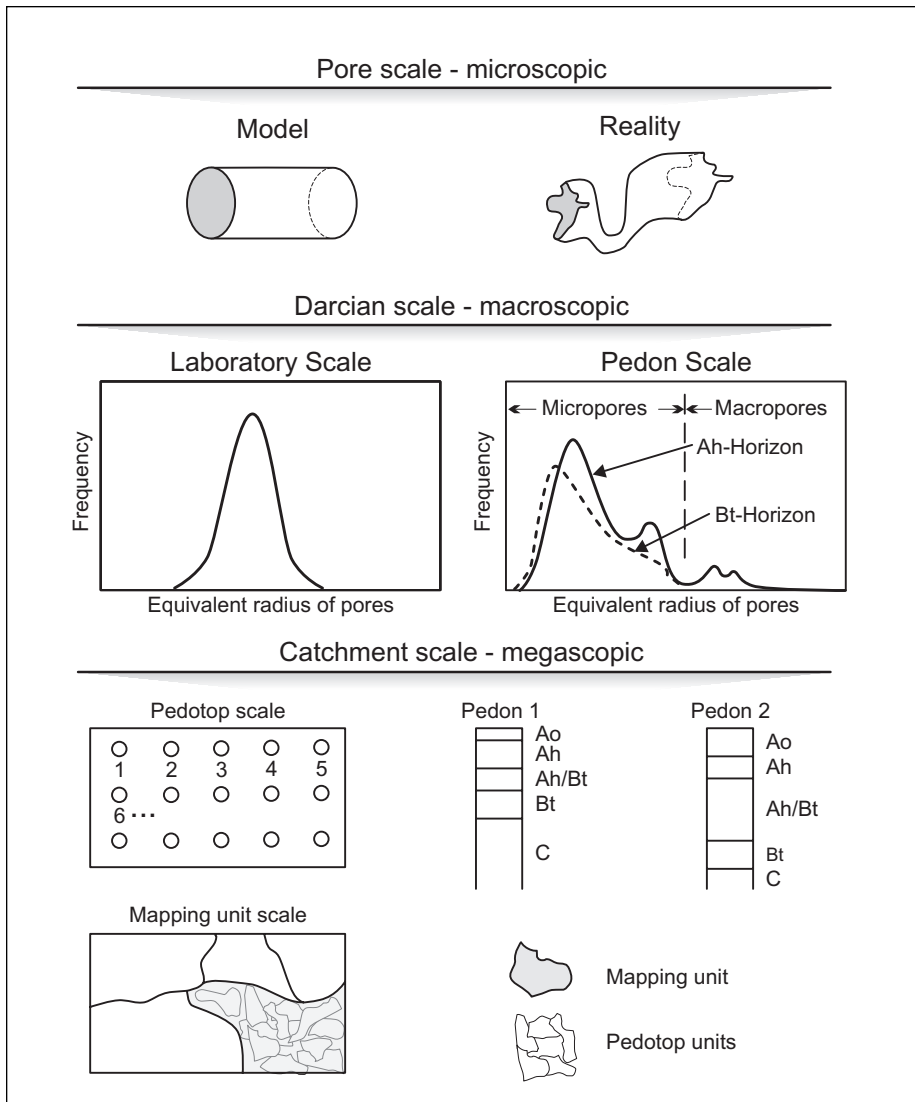


Figure 3-2. Scales in Soil Hydrology (Kutilek and Nielsen, 1994)

scale shown in Figure 3-3: (1) the pedotop scale, exhibiting a stochastic variability of the infiltration rate (Figure 3-3b), and (2) the mapping unit-scale, exhibiting mostly a deterministic variability (Figure 3-3c) of averaging infiltration rates within each mapping unit.

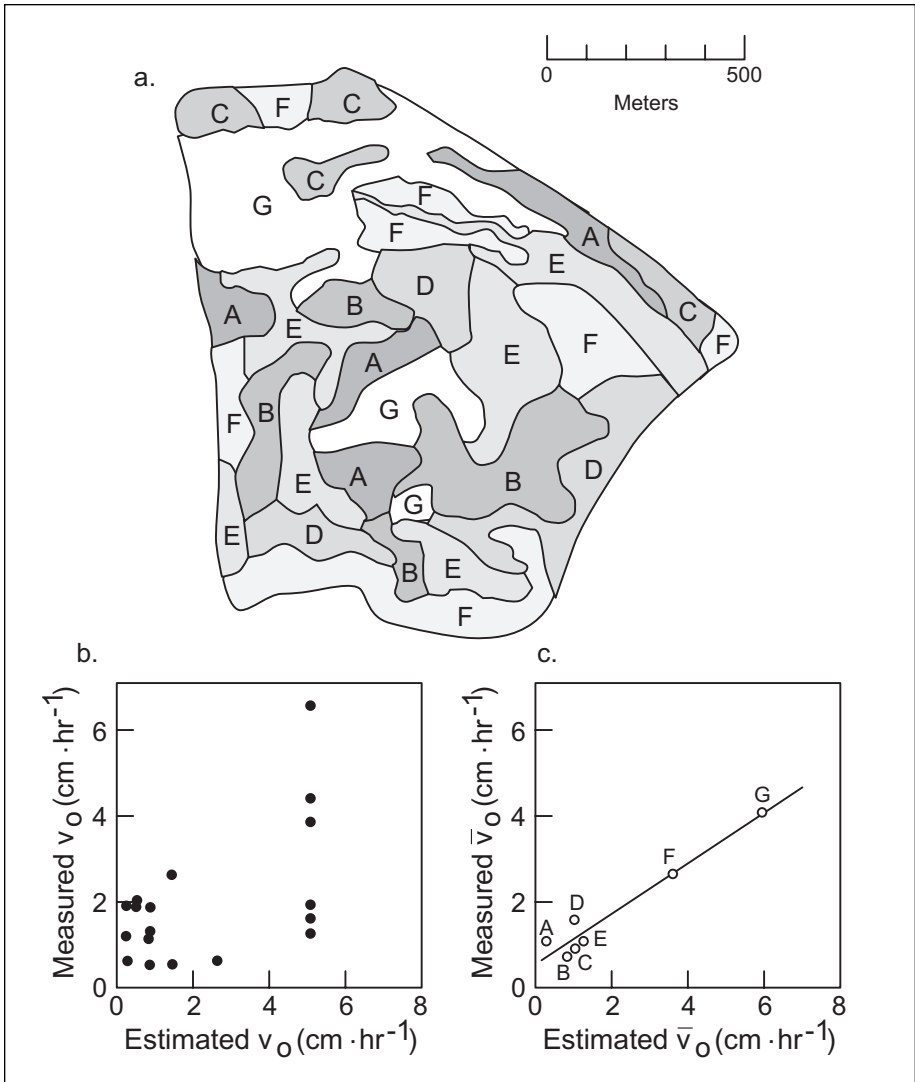


Figure 3-3. (a) Pedologic map delineating seven pedotops (designated A through G) within a mapping unit associated with a 100-ha farm. (b) Measured quasi-steady state infiltration rates for the seven pedotops illustrated in Figure 3-3a versus those estimated from soil texture. (c) Measured mean and estimated mean values \bar{v}_o within each pedotop (Kutilek and Nielson, 1994).

For flow in fractured rocks, Faybishenko *et al.* (1999b) proposed the following hierarchy (Figure 3-4) including elemental-scale, small-scale, intermediate-scale, and large-scale components.

Elemental components of the flow system include a single fracture or a block of porous medium (matrix). Elemental components range in size from a few centimeters to 10-20 cm. Elemental components can be studied in the laboratory using small core samples or larger fracture replicas or in the field using point-size probes. Results of experiments on this scale can be used to describe the details of specific flow and transport processes in fractures, in the matrix, or in fracture-matrix interactions. Some examples of these flow processes are: (1) water dripping from a

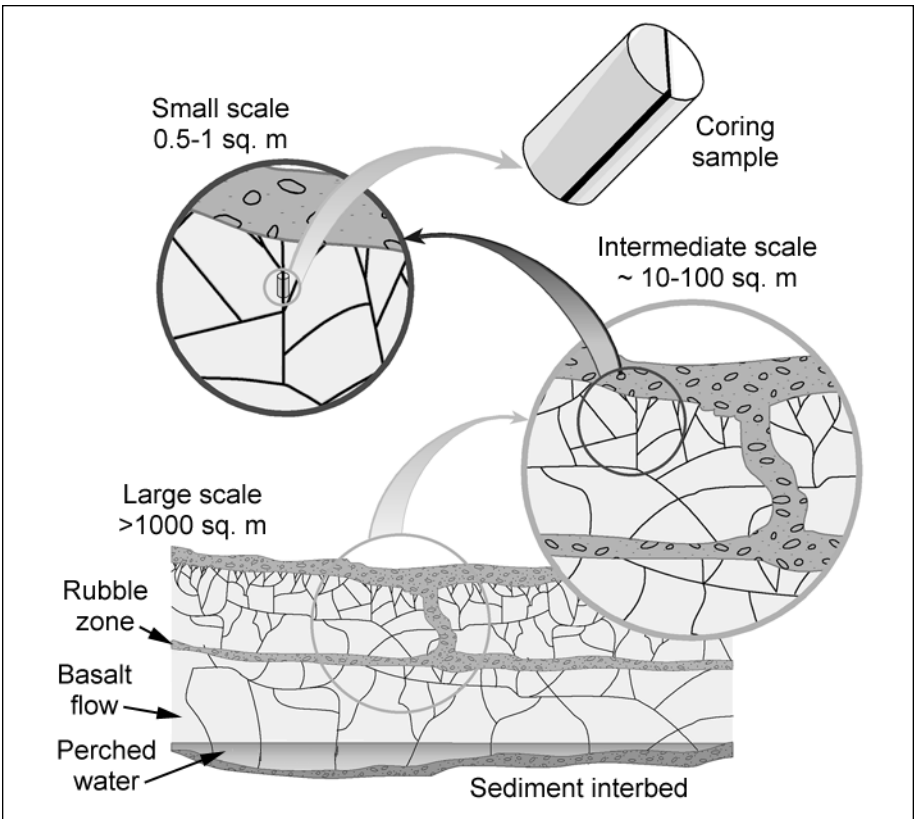


Figure 3-4. A four-level hierarchy of scales of hydrogeological components in fractured basalt (Faybishenko *et al.*, 1999)

fracture under field conditions in boreholes, tunnels, caves, and other underground openings; (2) film flow, or water meandering along a fracture surface; (3) water dripping within flow channels; and (4) intermittent flow along a fracture surface.

Small-scale components include a volume of rock within a single basalt flow with one or a few fractures. The areal extent of small-scale components is approximately 0.5–1 m². Results of field experiments on this scale can be used to describe in detail some of the flow and transport processes in a single fracture or a few intersecting fractures. Small-scale infiltration experiments are conducted to take into account fracture-matrix interaction, water-dripping phenomena, and small-scale averaging of flow rates and water pressures measured in fractures and matrix.

Intermediate-scale components include the volume of rock within a basalt flow involving all types of fractures, including the fractured flow top, dense flow interior, the less-fractured flow bottom, and fractures intersecting the basalt flow and rubble zone. The areal extent of intermediate-scale components is approximately 10–100 m². The results of field experiments at this scale can be used to describe all flow and transport processes within a single basalt flow. While our prime focus is the study of flow in the fracture network within a single basalt flow, we also study other basalt-flow features such as vesicular or massive basalt, fracture zones in the upper and lower fractured colonnade, and the central fractured zone or entablature.

Large-scale components involve the volume of rock containing several basalt flows and the rubble zones between them. The areal extent of a large-scale component usually exceeds 1,000 m². At this scale, we can study flow in the fracture networks and regional hydrogeological processes, which are affected by the network of vertical and horizontal rubble zones, as well as sedimentary interbeds.

Temporal Scales

Water fluxes and moisture profiles in the vadose zone depend on (a) short-term or event-based, (b) seasonal, and (c) long-term or climatic processes (Eagleson 1978; Milly and Egleson 1987). Assuming that the maximum rate of infiltration and exfiltration (evaporation) depends on the initial moisture content of soils, Reeves and Miller (1975), Milly (1986), and Salvucci and Entekhabi (1994) developed the Time

Compression Analysis (TCA) method to estimate the temporal mean moisture profiles of soils. However, Doodge and Wang (1993) demonstrated analytically that the TCA method is not exact.

It is important to determine temporal scales of vadose zone processes because we need to provide long-term predictions (up to hundreds and thousands of years) based on relatively short-term observations of several years. Because of the diurnal, seasonal, and annual variations of moisture content and water pressure at different depths, the vadose zone can be subdivided into several intervals (Figure 3-5). Field observations showed that the depth of these intervals remained approximately the same with time when the cycling of boundary (atmospheric) conditions was the same. Results identical to those of Kutilek and Nielsen (1994), as shown in Figure 3-5, were obtained by Faybishenko (1986), who studied a 44-meter-deep vadose zone in macroporous loam soils. Faybishenko determined that under ambient conditions (natural precipitation and snowmelt) in a semi-arid climate, four distinct zones appear along the vadose zone vertical profile: (1) a near-surface zone affected by episodic rain events, which extends from the surface to depths of 0.5 to 1 m; (2) a zone affected by seasonal infiltration, to depths of 6 to 8 m; (3) a zone of virtually constant moisture content, in which the hydraulic gradient is unity and there is annual downward water flow toward the aquifer; and (4) a capillary fringe zone above the water table. In these conditions, periodic downward and upward flow (as a result of evaporation) were observed in the upper two zones, and annual downward flow occurred below the depths of 6 to 8 m. However, changes in boundary (atmospheric) conditions, may affect the depths of these intervals. Field-observation results, such as these cannot be simulated using a one-dimensional flow model (Salvucci and Entekhabi 1994) because a one-dimensional model cannot describe the three-dimensional flow patterns that result from the deep penetration of water through preferential-flow zones immediately after precipitation, beyond the depth of a zone affected by evaporation. Thus, although the potential evapotranspiration exceeds the precipitation, downward water flow appears in arid and semi-arid climatic conditions (Faybishenko 1986; see also the case study “Near Surface Infiltration Monitoring Using Neutron Moisture Probes, Yucca Mountain, Nevada,” by Alan L. and Lorraine E. Flint). The observations summarized above also indicate that water is able to migrate

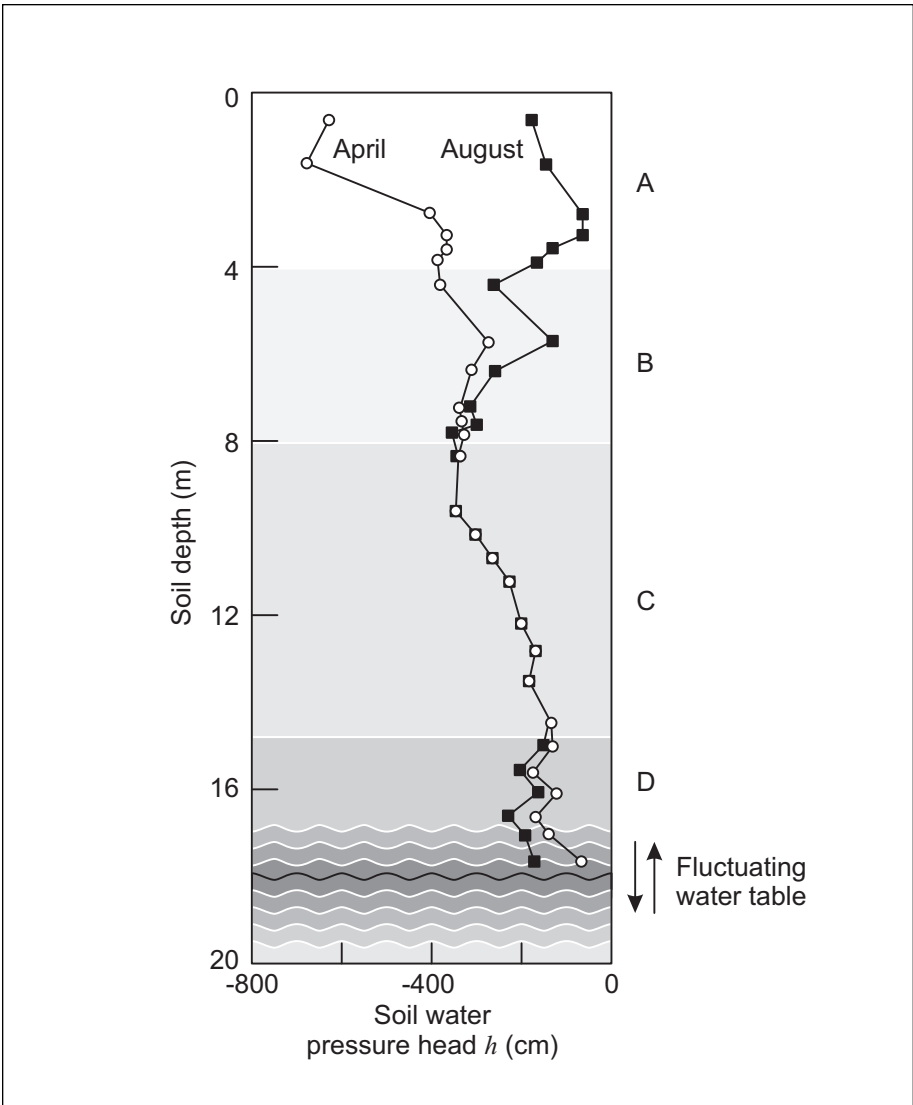


Figure 3-5. Monthly mean values of soil water pressure head h for two months of 1985 measured within the vadose zone of an irrigated soil in a semi-arid region of North China (Kutilek and Nielsen, 1994)

downward rather rapidly, along localized preferential flow paths in partially saturated soils and rocks, without being imbibed into the soil matrix.

Scaling of Hydraulic Parameters

Scaling theories assume that a continuously heterogeneous field is an ensemble of homogeneous domains with geometrical and soil hydraulic-function similarities. Scaling of hydraulic properties of heterogeneous soils was used by several authors (Warrick and Amoozegar-Fard 1979; Milly and Eagleson 1987; Bresler and Dagan 1979, 1983; Kabala and Milly 1991) to calculate water flow. Sposito and Jury (1990) showed that Richards' equation is invariant under the scaling transformation only if $K(\theta)$ is a power or exponential function. To demonstrate the usefulness of a scaling procedure, Figure 3-6 shows the results of water-content field measurements with time at four field plots at eight soil depths. (In total, 608 measurements, 19 times from 32 locations, were taken.)

However, obtaining volume-averaged fluxes by scaling the results of one-dimensional analysis to hydrologically connected and spatially heterogeneous fields is not a trivial task (Salvucci and Entekhabi 1994). Jury and Roth (1990) and Hewett and Behrens (1993) showed that the Miller-similitude assumptions and other scaling techniques may fail to represent heterogeneous soils. In studying fractured basalt, Faybishenko *et al.* (1999b) have found that, at each scale of investigation, different methods and models for flow phenomena must be used to explain observed behavior when no apparent scaling principles are evident.

Two case studies illustrating "Scaling of Soil Hydraulic Properties" by B.P. Mohanty and P.J. Shouse are on the accompanying CD.



EVIDENCE OF PREFERENTIAL FLOW IN HETEROGENEOUS SOILS AND FRACTURED ROCKS

Definition and Main Mechanisms of Preferential Flow

The term "preferential flow" is used to describe the flow that occurs in a non-volume-averaged fashion along localized, preferential pathways, by-passing a fraction of the porous space. Preferential flow in heterogeneous soils may occur along root channels, earthworm burrows,

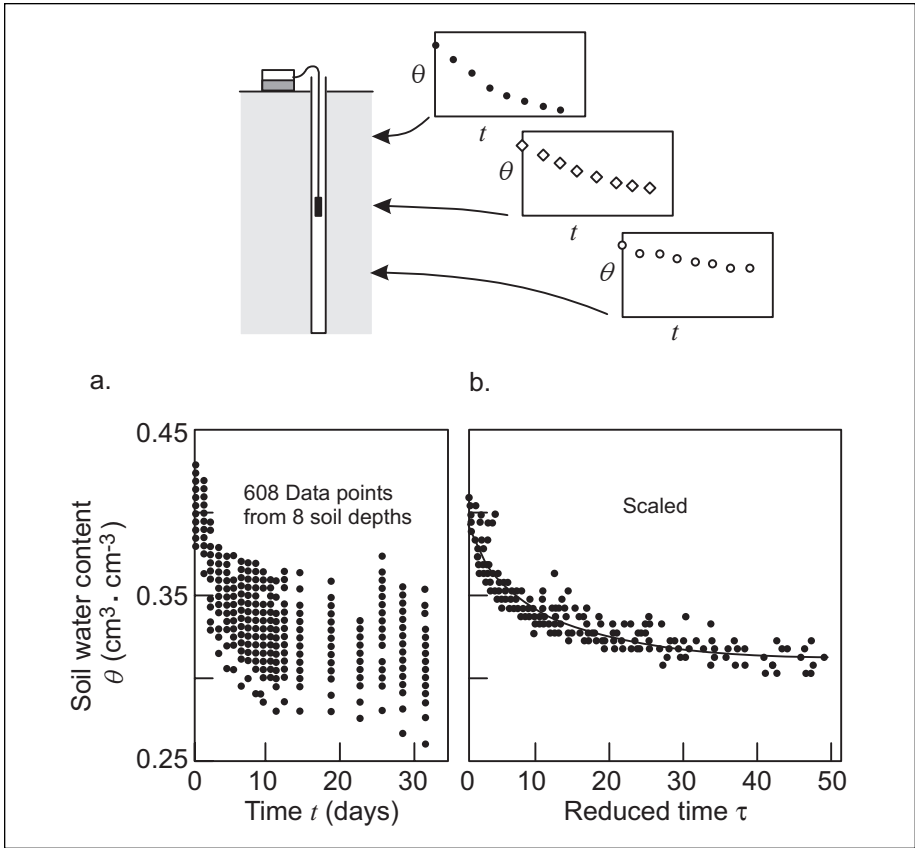


Figure 3-6. Neutron probe soil water contents measured at different soil depths and spatial locations during water redistribution. The solid line in figure c represents the scaled data given in Kutilek and Nielsen (1994, page 265)

and soil fissures or cracks in both fine-textured and coarse-textured soils, as well as at geological heterogeneities such as fractures, clastic dikes, and breaks in caliche layers. Such heterogeneities are created as a result of depositional conditions, diagenesis of sediments, faulting, fracturing, and differential weathering processes. Because flow velocity is higher along the zones of preferential flow than in other parts of the media, preferential flow is also called “fast flow”.

Water seepage in the subsurface depends on the state of the land surface, the heterogeneity of the soil profile, and characteristics of the atmospheric and artificial forcing events, which occur on different time scales. Figure 3-7a schematically illustrates several types of fluxes at the

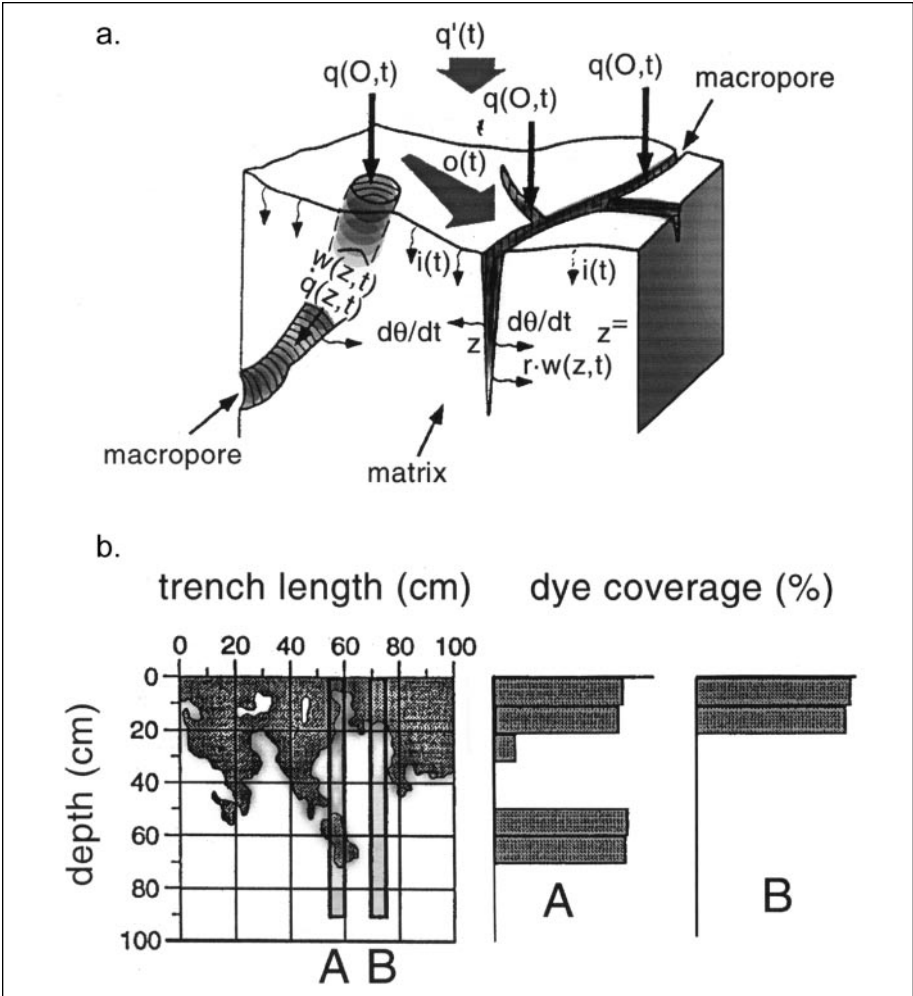


Figure 3-7. Illustration of a concept of preferential flow in heterogeneous soils: (a) Schematic of fluxes occurring under infiltration: $q^*(t)$ is overall water input - precipitation and irrigation, $i(t)$ is infiltration into the top soil matrix, $o(t)$ is overland flow (runoff) when $q^*(t) > i(t)$, $q(O,t)$ is volume flux density into the soil macropores, $q(z,t)$ is volume flux density, $w(z,t)$ is the volumetric soil moisture content, $r \cdot w(z,t)$ is the water sorbance from macropores into the soil matrix (Germann and Beven, 1990). (b) Map of the two-dimensional distribution of a chemical at the excavated trench exposure after sprinkling 40-mm dye solution onto the soil surface, and percent of a chemical at different depths determined using cores in vertical wells A and B (Flury, 1996).

land surface causing the phenomenon of preferential flow in macroporous soils and the water redistribution between the macropores and the matrix, and Figure 3-7b depicts a distribution of the dye tracer along the vertical cross-section of the structured, fine-textured soil. Small changes in the water-flow regime of a heterogeneous, deep vadose zone may not be inferred from conventional moisture-content measurements (for example, using neutron logging), because the accuracy of measurements is within range of the moisture-content fluctuations. We can overcome this problem with long-term field measurements of the water pressure using deep tensiometers.

Several mechanisms are assumed to cause preferential flow, including water repellency, cracks, biological effects (such as earthworm or root channels and macropores), air entrapment, small-scale variations in soil hydraulic properties, discrete obstacles, entrapped air behind the wetting front, and confined air ahead of the wetting front. Field infiltration tests with tracers showed that the volume of wetted soils within fingers could occupy from as little as 2% (Kung 1990a,b) to as much as 70% of the total volume of soil (Jury *et al.* 1986; Ghodrati and Jury 1990). This knowledge is important in predicting the fate of contaminants. Small differences in surface topography may significantly affect spatial variations of infiltration, which occur as a result of non-uniform snowmelt on the land surface and changes in soil hydraulic properties in the near-surface zone (for example, resulting from temperature variations). Preferential flow in the vadose zone creates localized groundwater recharge, which may vary with time as a result of changes in the chemical composition of moving and indigenous solutes. For example, sodium concentration, redox conditions, biological transformation of organic materials, and high temperature may significantly affect hysteretic properties of water retention and unsaturated hydraulic conductivity of unsaturated-saturated soils, as well as the processes of water, chemicals, and bio-transformation between the zones of fast flow paths and slow volume-averaged flow.

The capillary characteristics of the heterogeneous sands play a critical role in the displacement of water by a dense, immiscible phase, chlorinated solvent such as a dense nonaqueous phase liquid, or DNAPL (Chen *et al.* 1995; Ewing and Berkowitz 1998). The invading DNAPL may flow laterally and cascade off fine-sand lenses (Kueper *et al.* 1989). Chilakapati *et al.* (1998) showed that the prediction of geochemical transport in

heterogeneous systems using a volume-averaged model significantly underestimated oxidation the reaction kinetics, and retardation.

Examples of Preferential Flow in Soils and Fractured Rocks

Heterogeneous Soils and Sediments at the Hanford Site

The sediments beneath waste sites at Hanford are highly heterogeneous (for example, sediments include interbedded sand, silts, gravels, and boulders). Temporal and spatial variations in net water infiltration through current and past liquid discharges, water line leaks, and variable chemical interactions complicate description and understanding of contaminant transport, and lead to uncertainty in the evaluation of transport at contaminated sites. A number of knowledge gaps—including an insufficient understanding of source terms, geological and hydrologic properties, preferential flow, and chemical interactions—make current modeling of contaminant transport in the Hanford vadose zone unreliable.

Figure 3-8 presents an example of three potential types of preferential flow in the vadose zone identified at the DOE Hanford site: (1) fingering, (2) funnel flow, and (3) flow associated with clastic dikes or poorly sealed borehole annular space. According to Ward *et al.* (1997), funnel flow can enhance lateral migration, and horizontal layering will tend to stabilize fingered flow, whereas cross-bedding concentrates and coalesces fingers (Glass *et al.* 1991; Glass and Nicholl 1996; Nicholl *et al.* 1993). Flow through clastic dikes and poorly sealed well-annular spaces could exhibit a hysteretic effect: it may appear during infiltration events, and there may be flow impediments during drying.

A more detailed description of transport beneath Hanford waste tanks is given in “Gamma Borehole Logging for Vadose Zone Characterization Around the Hanford High-Level Waste Tanks” by D.S. Shafer, J.F. Bertsch, C.J. Koizumi, and E.D. Fredenburg. *See page 445.*



Fractured Basalt at the Idaho National Engineering and Environmental Laboratory (INEEL) Site

Percolation ponds, injection wells, and buried waste sites are primary sources of fractured-basalt vadose zone contamination at INEEL. The

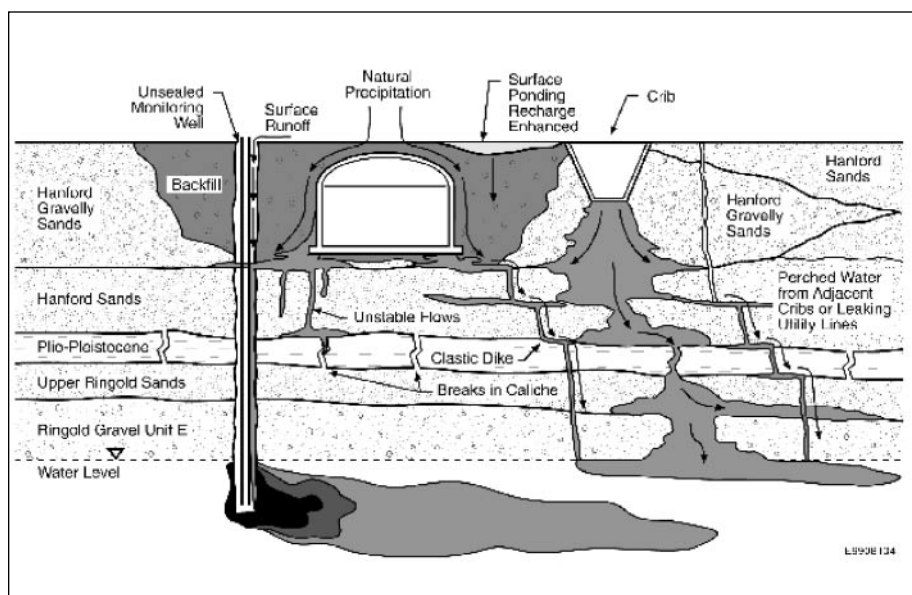


Figure 3-8. Conceptual model of fluid flow beneath single shell tanks at Hanford showing fingering, funnel flow, and flow associated with clastic dikes or poorly sealed borehole annular space (DOE 1999).

Radioactive Waste Management Complex (RWMC) includes one of the largest subsurface waste disposal facilities in the Department of Energy (DOE) complex. In the past, disposal of low-level, mixed, and transuranic radioactive wastes was achieved by direct discharge or burial in shallow, unlined pits and trenches within the surficial sediments. Vadose zone fractures provide a mechanism for deep transport of oxidizing fluid and gas, leading to the release of toxic species, such as heavy metals, that may otherwise be stable in a reducing environment. Flooding of the RWMC has occurred three times in the past, potentially increasing the downward mobility of the subsurface contaminants. The determination of the time required for contaminants to reach the aquifer is important to decision-making regarding remediation options. In 1994, INEEL conducted a Large Scale Infiltration Test (LSIT) 1.4 km south of

RWMC to investigate hydrologic properties of the vadose zone basalts. The vadose zone thickness near the RWMC is about 190 m. The LSIT site consisted of a bermed basin, 183 m in diameter, which contained 32 million L of water. Beneath the basin is a thick sequence of stacked basaltic lava flows, with the first major interbed at a depth of 55 m. Seventy wells were drilled for the test, primarily along four axes extending radially from the basin, with most terminating in the sedimentary interbed. During the LSIT, tracers did not always follow the same pathways as the initial water movement. The tracer distribution could not be modeled as a one-dimensional steady-state flow, but rather as a three-dimensional network of flow paths, which may vary in time (Wood and Norrell 1996; Faybishenko *et al.* 1999a,b).

The case study "Large-Scale Field Investigations in Fractured Basalt in Idaho: Lessons Learned," by Boris Faybishenko and Thomas Wood, discusses the results and lessons learned from Large Scale Infiltration Tests at the National Engineering and Environmental Laboratory. *See page 396.*



Other Sites

The observations at Hanford and INEEL are in agreement with a growing body of field evidence from various sites in semi-arid regions in the U.S.A. and throughout the world (for example, Yucca Mountain [Flint and Flint 1995], Arizona [Wierenga *et al.* 1998], New Mexico [Wierenga *et al.* 1991; Hills *et al.* 1991], Australia [Allison 1988], and Israel [Nativ *et al.* 1995]. These investigations show that water seepage occurs in an episodic manner along localized preferential pathways at depths of several hundred meters beneath the land surface. It is important to note that only portions of fractures carried water, and the chemical composition of water obtained from fractures was substantially different from that of water samples extracted from the nearby rock matrix (Eaton *et al.* 1996). At a field site in the Negev Desert, Israel, man-made tracers were observed to migrate with velocities of several meters per year across an unsaturated zone of fractured chalk 20 to 60 m in thickness (Nativ *et al.* 1995).

CONTAMINANT TRANSPORT

Point and Linear Source Contaminants

Point-source pollutants are associated with leakage from surface and underground tanks, injection of nuclear and organic wastes in boreholes screened at different depths in the vadose zone, surface spills, etc. Pollution is often highly toxic near the point source, but the exact location of the source is often not easily detectable. Linear-source contaminants enter the vadose zone from sewers, trenches, cribs, creeks, and rivers. Contaminant movement from the source often follows zones of preferential flow, which are difficult, if not impossible, to identify in heterogeneous soils and fractured rocks.

Non-Point Source Contaminants

Non-point-source (NPS) pollutants include contaminants in soils, sediments, and surface waters (such as organic and radioactive materials, fertilizers, pesticides, salts, and metals), that are wide-spread over large areas. Contamination of soil and water resources by NPS pollutants is a major global environmental issue, because the pollutant distribution is not limited by geological and physical boundaries such as lakes, rivers, and mountains. Therefore, the extent of NPS contamination and associated chronic health effects are major environmental threats (Corwin 1996).

NPS pollution of surface waters is caused by surface runoff and erosion. The increase in NPS pollutants is usually a result of human activities including agriculture, urban runoff, feedlots, atmospheric pollution, water-resource extraction, and waste storage. The areal extent of NPS contamination in heterogeneous soils and sediments increases the complexity and volume of data required for assessment far beyond that of typical point-source pollutants. Because of the uncertainty associated with the regional-scale assessment of NPS pollutants, the design of site-characterization and monitoring methods poses complex technical problems (Loague and Corwin 1996).

Contaminant Transport Processes

Contaminants can be present in soils in all three phases—liquid, solid, and gaseous. The main transport processes of contaminants in a

liquid phase are advection, dispersion, sorption-desorption, ion exchange, and decay reactions. Hydrodynamic dispersion is the process affected by molecular diffusion caused by a concentration gradient, together with dispersion caused by mechanical mixing and fluid advection. The simplest approach to the contaminant-transport investigation is to consider miscible migration of nonvolatile reactive compounds in the liquid phase, which can be sorbed by the solid phase (Figure 3-9).

The liquid flowing through the soil is not pure water but, even with a single chemical dissolved, a complex fluid (Sposito 1981). Sposito (1981) and Nkedi-Kizza *et al.* (1985) demonstrated how to evaluate the enhanced solubility of chemicals affected by the solvent chemical properties. Figure 3-10 shows the impact of the mixed solvents on the retardation factor. It is important to note that the co-solvent may decrease the retardation factor by several orders of magnitude and, therefore, may enhance the migration of toxic chemicals in soils and groundwater. The impact of the co-solvent (for example, methanol or acetone) is greater

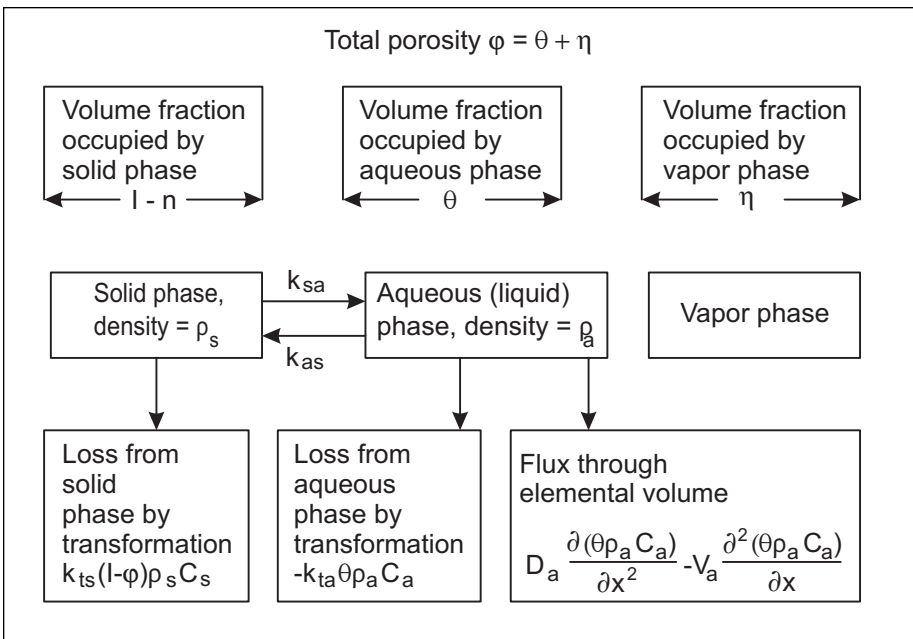


Figure 3-9. Conceptual model showing the transport processes of miscible nonvolatile reactive compounds in soils (Enfield and Yates, 1990)

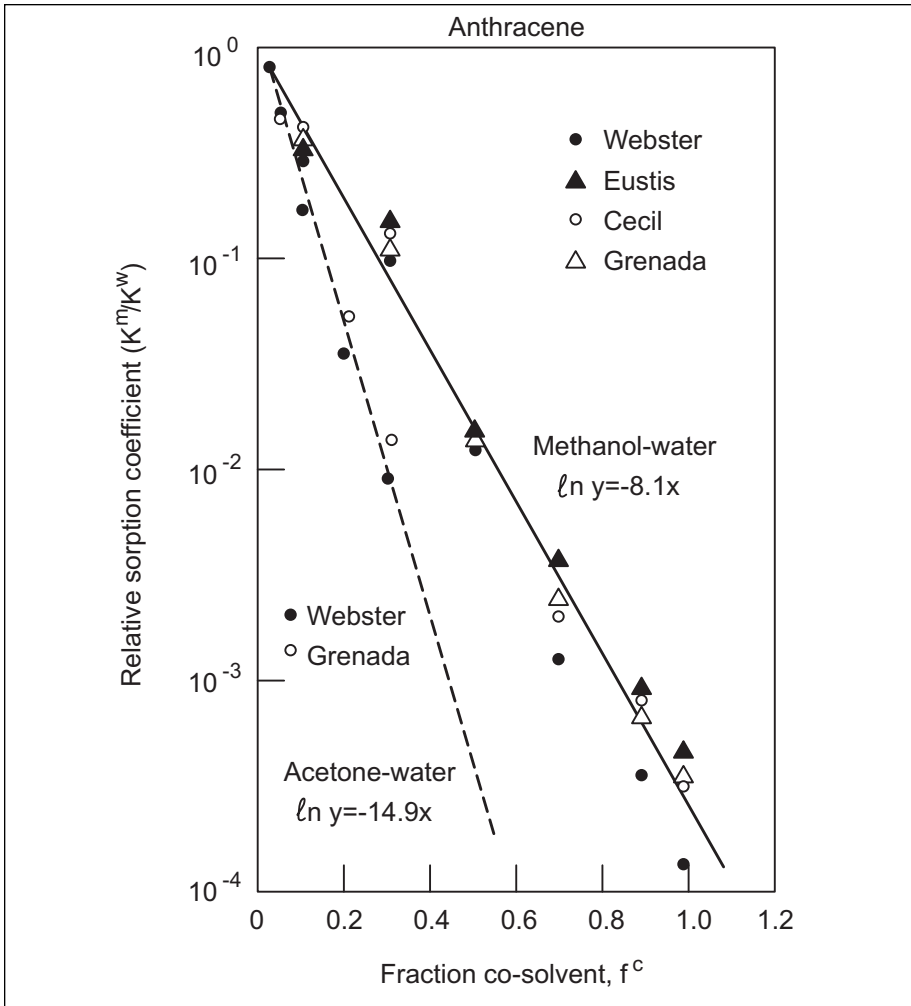


Figure 3-10. Graphs illustrating that the retardation factor decreases several orders of magnitude as the fraction of mixed solvents increases (Nkedi-Kizza *et al.*, 1985)

for more hydrophobic chemicals (Nkedi-Kizza *et al.* 1985). Chemical transport in soils and groundwater can be enhanced by immiscible fluids, or surfactants. Figure 3-11 conceptualizes a number of multi-phase flow and transport processes in soils, which one should take into account in designing characterization and monitoring methods for the vadose zone.

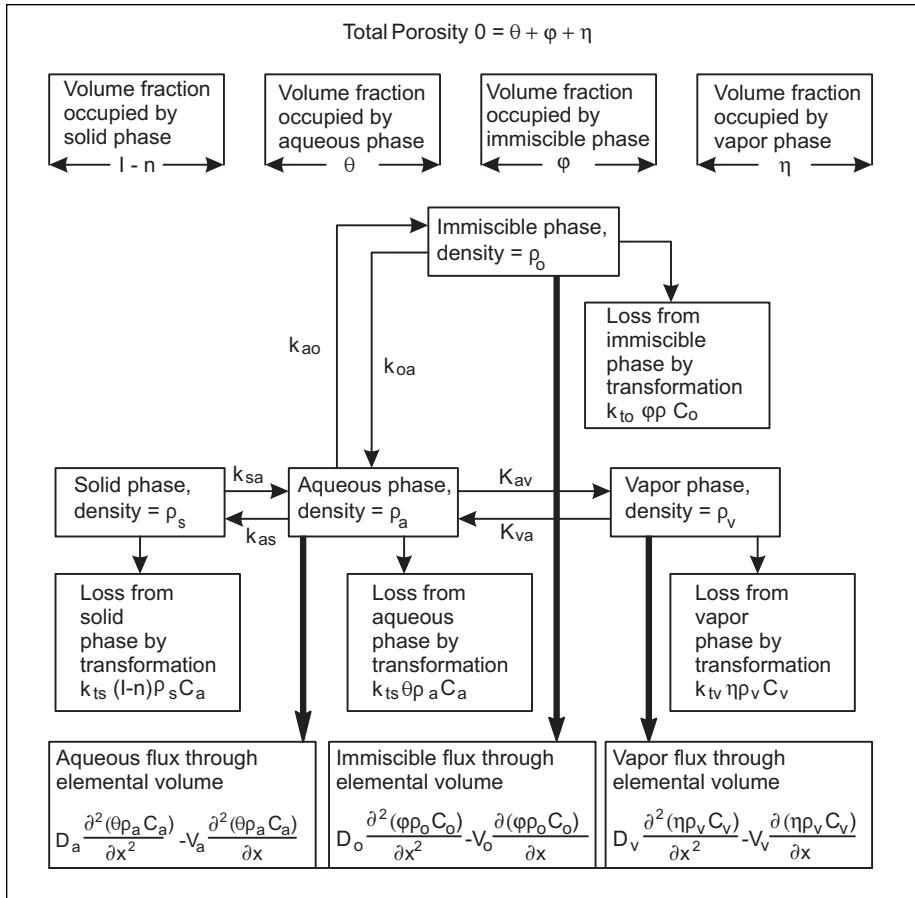


Figure 3-11. Conceptual model indicating the transport processes of multiple fluid phases in soils (Enfield and Yates, 1990)

In structured soils, the macropores can significantly influence movement of volatile compounds because open macropores constitute pathways for vapor-phase movement both downward to the water table and upward from the water table to the atmosphere. Under arid conditions, when the liquid flow in dry soils is insignificant, diffusion and advective transport in the vapor phase may be many times greater than diffusion in the liquid phase.

Figure 3-12 shows a general structure of the system of first-order decay reactions for three solutes (A, B, and C) adopted from Simunek

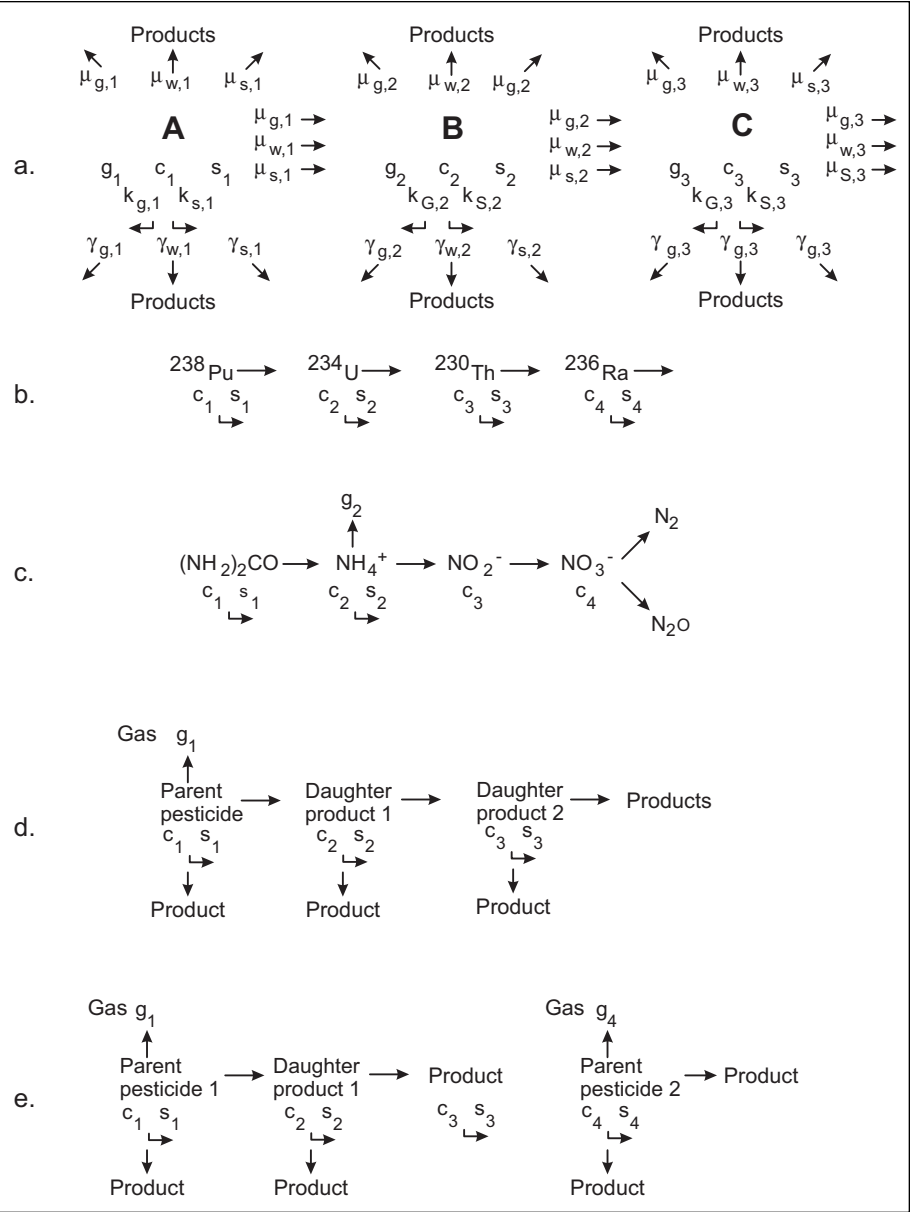


Figure 3-12. First-order decay reactions in soils: (a) a general structure of the system for three solutes (A, B and C), and typical examples of first-order decay reactions for (b) radionuclides, (c) nitrogen, (d) pesticides with interrupted chain (one reaction path), and (e) interrupted chain (two independent reaction paths) (Simunek and van Genuchten, 1995)

and van Genuchten (1995). This figure also shows typical examples of first-order decay reactions for radionuclides, nitrogen, and pesticides. However, the oxidation processes in groundwater may be second-order, depending on the concentration of oxygen (Borden and Bedient 1986). Additional investigations are needed to better understand the second-order reaction processes and determine how chemical reaction coefficients depend on environmental variables such as O_2 , pH, temperature, and nutrients affecting the biochemistry.

The assumption of decoupling water flow from chemical transport is not always adequate, especially in geothermal fields where temperature gradients can create density-driven mass transport and affect the unsaturated hydraulic properties of soils. Because of heat generation and significant temperature gradients, the effect of temperature on liquid, vapor, and chemical transport should be taken into account in predicting contaminant transport (for example below Hanford tanks).

Another mechanism affecting contaminant behavior in the vadose zone is colloidal migration of contaminants. Colloids are usually present in soils as suspended substances that facilitate transport of both organic and radioactive contaminants. Mobility of colloids depends on liquid flow velocity and on chemical interactions between colloids and matrix surfaces. Although colloidal transport plays an important role in contaminant migration in partially saturated soils, until now only a few studies addressed this problem on the field scale.

BIOLOGICAL PROCESSES*

Terminology

Bioremediation is the use of biological processes to make the environment less toxic. More specifically, bioremediation, uses enzymes, growth stimulants, bacteria, fungi, or plants to degrade, transform, sequester, mobilize, or contain contaminant organics, inorganics, or metals in soil, water, or air. Thus, characterization and monitoring of bioremediation can be performed by measuring the number and type of microorganism, enzymes, or other biochemical markers, breakdown

*This section was contributed by T.C. Hazen.

products, or metabolic indicators (for example, CO_2). To assist in defining characterization and monitoring opportunities, we summarize bioremediation terminology in Table 3-1.

Engineered Bioremediation Concepts and Objectives

Bioremediation systems can be roughly divided into natural attenuation (or intrinsic remediation) and engineered systems. Monitoring needs are directly related to the approach and objective selected for a site. All engineered bioremediation can be characterized as either biostimulation (that is, the addition of nutrients), bioaugmentation, (that is, the addition of organisms), or as a process that uses both. The problems related to adding chemical nutrients to sediment and groundwater are fundamentally different from those related to adding organisms. Simple infiltration in soils and, subsequently, groundwater is physically quite different in the two processes (Alfoldi 1988). Even the smallest bacteria have different transport properties than chemicals. For example, clayey soils have very low permeability and physically may not allow bacteria to penetrate. These clays also may bind the microbes that are added (for example, as cationic bridges, involving divalent metals and the net negative charge on the surface of the bacteria and the surface of the clay, are formed). In some soils, inorganic chemicals that are injected may precipitate metals, swell clays, and change redox potentials and conductivity, thus having a profound effect on groundwater flow and the biogeochemistry of the environment.

Natural attenuation and biostimulation depend on the indigenous organisms. Thus, these methods require that the correct organisms are present in sufficient numbers. In addition, for biostimulation, we must alter the environment in a way that will have the desired bioremediation effect. In most terrestrial subsurface environments, the indigenous organisms have been exposed to the contaminant for extended periods of time and have adapted (for example, through natural selection). Many contaminants, especially organic compounds, are naturally occurring or have natural analogs in the environment. Rarely can a terrestrial subsurface environment be found that does not already have a number of organisms that can degrade or transform any contaminant present. Indeed, even in pristine environments, bacteria have an increasing number of plasmids (small extrachromosomal bits of DNA that code for

TABLE 3-1 Terminology Related to Bioremediation

Bioaugmentation—The addition of organisms to effect remediation of the environment (for example, the injection of contaminant-degrading bacteria into an aquifer)

Bioavailability—The ability of a compound or element to be used by a living organism. Some compounds lack bioavailability because they are insoluble, strongly sorbed to solids, or, for some other reason, they cannot be utilized as a source of nutrients or energy.

Biocurtain—The process of creating a subsurface area of high biological activity to contain or remediate contaminants

Biodegradation—A biological process of reducing a compound to simpler compounds, which may be either complete (for example, reducing organic compounds to inorganic compounds) or incomplete (for example, removing a single atom from a compound)

Biofilters—Normally used to refer to treatment of gases by passing them through a support material containing organisms, such as soil, compost, or trickle filter; sometimes also refers to treatment of groundwater via passage through a biologically active area in the subsurface

Bioimmobilization—A biological treatment process that involves sequestering the contaminant in the environment, but involves no biodegradation of the contaminant

Biological Treatment—Any treatment process that involves organisms or their products; for example, enzymes

Biomobilization—A biological treatment process that makes the contaminant more mobile in the environment, but involves no biodegradation of the contaminant.

Biopiles—Above-ground mounds of excavated soils that are biologically treated by addition of moisture, nutrients, air, or organisms

Bioreactor—A contained vessel (such as a fermentor) in which biological treatment takes place

Bioremoval—A biological treatment involving uptake of the contaminant from the environment by an organism or its agent

Bioslurping—Soil vapor extraction combined with removal of light nonaqueous phase liquid contami-

nants from the surface of the groundwater table, thereby enhancing biological treatment of the unsaturated zone and the groundwater, especially the capillary fringe zone

Bioslurry Reactor—Biological treatment of soil-bound and water-soluble contamination by making a thin mixture with water (a "water slurry") and treating the mixture in a contained vessel

Biosparging—Injection of air or specific gases below ground (usually into saturated sediments (aquifer material) to increase biological rates of remediation

Biostimulation—The addition of organic or inorganic compounds (for example, fertilizer) to cause indigenous organisms to effect remediation of the environment

Biotransformation—A biological treatment process that involves changing aspects of contaminants, such as the valence states of metals, the chemical structure, and so on

Bioventing—Originally defined as slow vapor extraction of contaminants from unsaturated soils to increase flow of air into the subsurface via vents or directly from the surface, thus increasing aerobic biodegradation rates; now defined more broadly to include the slow injection of air into unsaturated soils

Composting—Treatment of waste material or contaminated soil by aerobic biodegradation of contaminants in an above-ground, contained, or uncontained environment

Engineered Bioremediation—Any type of manipulated, stimulated, or enhanced biological remediation of an environment

Intrinsic Bioremediation—Unmanipulated, unstimulated, unenhanced biological remediation of an environment (that is, natural biological attenuation of contaminants in an environment)

Land Farming—A process of biologically treating uncontained surface soil, usually by aeration of the soil (tilling) and addition of fertilizer or organisms

Prepared Beds—A contained (lined) area above ground where soil can be tilled or variously manipulated to increase biological remediation; that is, contained land farming

enzymes that can degrade complex compounds like antibiotics) with sediment depth, in response to the increasing recalcitrance of the organics present (Fredrickson *et al.* 1988).

Our ability to enhance bioremediation of any environment is directly proportional to our knowledge of the biogeochemistry of the site. Finding the limiting conditions for the indigenous organisms to carry out the desired remediation is the most critical step. As with surface environments, the parameters that usually limit organisms are required nutrients, inorganic and organic. The most common nutrients are water, oxygen, nitrogen, and phosphorus. In the terrestrial subsurface, water can be limiting, but usually is not. Oxygen is quite often limiting since contaminants can be used as carbon and energy sources by organisms and the contaminant concentration greatly exceeds the oxygen input needed by the organisms. Introduction of air, oxygen, or hydrogen peroxide via infiltration galleries, tilling, sparging, or venting have proven to be extremely effective in bioremediating petroleum contaminants and a variety of other organic compounds that are not particularly recalcitrant (Thomas and Ward 1992). However, if the environment has been anaerobic for extended periods of time and the contaminant has a high carbon content, it is likely that denitrification has reduced the overall nitrogen content of the environment, making this nutrient limiting. Nitrogen has been successfully introduced into the terrestrial subsurface for biostimulation using ammonia, nitrate, urea, and nitrous oxide (EPA 1989). Phosphorus is naturally quite low in most environments and, in terrestrial subsurface environments, even if concentrations are high, the phosphorous may be in a mineral form that is biologically unavailable, such as apatite. Several inorganic and organic forms of phosphate (for example, triethyl phosphate, phosphoric acid, sodium phosphate), have been successfully used to biostimulate contaminated environments (EPA 1989, Hazen 1997). In environments where the contaminant is neither a good carbon nor energy source and other sources of carbon or energy are absent or unavailable, it will be necessary to add an additional source of carbon (Horvath 1972). An additional source of organic carbon will also be required if the total organic carbon concentration in the environment falls below 1 ppm and the contaminant cleanup levels have still not been met. Methane, methanol, acetate, molasses, sugars, agricultural compost, phenol, and toluene have all been added as secondary carbon supplements to the terrestrial subsurface to stimulate

bioremediation (National Research Council 1993). Even plants such as poplar trees have been used to biostimulate remediation of subsurface environments (Schnoor *et al.* 1995).

The plants act as solar-powered nutrient pumps that stimulate rhizosphere microbes to degrade contaminants (Anderson *et al.* 1993).

Biostimulation strategies are limited most by our level of ability to deliver the required stimulus to the environment. The permeability of the formation must be sufficient to allow perfusion of the nutrients and oxygen through the formation. The minimum average hydraulic conductivity for a formation is generally considered to be 10^{-4} cm/sec (Thomas and Ward 1989). Additionally, the stimulants required must be compatible with the environment. For example, hydrogen peroxide is an excellent source of oxygen, but it can cause precipitation of metals in soils and lead to such dense microbial growth around the injection site that all soil pores are plugged. It is also toxic to bacteria at high concentrations, for example, above 100 ppm (Thomas and Ward 1989). Ammonia also can be problematic, because it adsorbs rapidly to clays, causes pH changes in poorly buffered environments, and can cause clays to swell, decreasing permeability around the injection point. At some sites, many of these problems can be handled by excavating the soil or pumping the groundwater to the surface and treating it in a bioreactor, prepared bed, land farm, bioslurry reactor, biopile, or compost. In these cases, the permeability can be controlled or manipulated to allow better stimulation of the biotreatment process. It is generally accepted that soil bacteria need a C:N:P ratio of 30:5:1 for unrestricted growth (Paul and Clark 1989). Stimulation of soil bacteria can generally be achieved when this nutrient ratio is achieved following amendment addition. The actual injection ratio used is usually slightly higher (a ratio of 50:5:1), since these nutrients must be bioavailable, a condition that is much more difficult to measure and control in the terrestrial subsurface (Litchfield 1993). It may also be necessary to remove light nonaqueous phase liquid (LNAPL) contaminants that are floating on the water table or smearing the capillary fringe zone, hence bioslurping (Keet 1995). This strategy greatly increases the biostimulation response time by lowering the highest concentration of contaminant the organisms are forced to transform.

Bioaugmentation may provide significant advantages over biostimulation for: (1) environments where the indigenous bacteria have not had time to adapt to the contaminant; (2) particularly recalcitrant contami-

nants that only a very limited number of organisms are capable of transforming or degrading; (3) environments that don't allow a critical biomass to establish and maintain itself; (4) applications where the desired goal is to plug the formation for contaminant containment, such as a biocurtain; and (5) controlled environments where specific inocula of high-rate degraders will greatly enhance the process (for example, bioreactors, prepared beds, composting, bioslurry reactors, and land farming). Like biostimulation, a major factor affecting the use of bioaugmentation in the terrestrial subsurface is hydraulic conductivity. The 10^{-4} cm/sec permeability limit for biostimulation will need to be an order of magnitude higher for bioaugmentation and may need to be higher yet, depending on the size and adherence properties of the organism being applied (Baker and Herson 1990). Recent studies have shown that the less adherent strains of some contaminant-degraders can be produced, allowing better formation penetration (DeFlaun *et al.* 1994). However, the ability to rapidly clog a formation is a significant advantage of bioaugmentation in applications where containment is a primary goal. The oil industry has been using this strategy for a number of years to plug fluid loss zones and enhance oil recovery (Cusack *et al.* 1992).

Bioaugmentation is indistinguishable from biostimulation in many environments, since nutrients are often injected with the organisms and since dead organisms are an excellent source of nutrients for most indigenous organisms. For many applications it is difficult, if not impossible, to determine if the added organisms *provide* a significant advantage over nutrient stimulation alone. Even some of the best controlled bioaugmentation field studies, such as the caisson studies of polychlorinated biphenyl (PCB) biodegradation in Hudson River sediment, could not show a significant advantage for bioaugmentation over biostimulation alone (Harkness *et al.* 1993). Given the problems and high cost of producing and delivering the organisms, bioaugmentation applications will probably remain limited. However, bioaugmentation may have a very significant advantage when genetically engineered microorganisms (GEMs) are used. It is possible that a GEM could be constructed with unique combinations of enzymes to facilitate sequential biotransformation or biodegradation of a contaminant. Such a microorganism would be particularly helpful for contaminants that are extremely recalcitrant (such as PCBs), or are degraded only under limited conditions (for example, tetrachloroethylene and carbon tetrachloride can only be

biodegraded anaerobically). In addition, a GEM could be modified with unique survival or adherence properties that would make it better suited to the environment where it was to be applied.

FIELD VADOSE ZONE CHARACTERIZATION AND MONITORING

TYPES OF DATA FOR SITE CHARACTERIZATION AND MONITORING METHODS

Site Selection

An important step in developing a program for site characterization and monitoring is the selection of the appropriate field site location. The selection of the field site should focus primarily on the detection and characterization of contaminant source areas and existing and potential pathways for contaminant transport in the subsurface. Under the Resource Conservation and Recovery Act (RCRA) of 1976, waste management facilities are required to obtain permits to begin field characterization. The selection of the field site usually starts with a preliminary review of existing information on the facilities in order to identify and characterize existing and potential releases. The next step is a visual inspection of the entire facility for evidence of releases and identification of additional areas of concern. Following the inspection, a plan is developed for the sampling visit, and additional information needed to identify the areas affected by contaminant releases is collected to fill data gaps needed to identify the areas affected by contaminant releases. This information, in combination with basic site characterization data (that is, topography, soils, geology, hydrology, and biota and current and past land use and ownership), is used to determine site boundaries and the monitoring system layout.

While site boundaries may be initially defined by ownership, a broader scale should be evaluated to determine the need for the offsite investigation. For example, investigations of vadose zone and groundwater contamination should include areas of potential release sources located upgradient as well as potential migration paths located downgradient from a site. The boundaries of the area investigated can be changed or extended with time when new information on the extent of contamination becomes available. The case study “Groundwater Contamination in the Perched Aquifer at the DOE Pantex Plant: Successful Characterization Using the ESC Approach,” by Caroline Purdy and

Jacqueline C. Burton, gives an example of using new information to manage decision-making about changing the areal extent of contamination at a field site.

Characterization of Natural Conditions

Characterization of natural (ambient background or baseline) conditions involves the following tasks:

- Locating, collecting, and organizing basic types of data from available published and unpublished sources
- Conducting specifically designed field, laboratory, and modeling studies for the sites selected
- Using the information from natural analogue sites.

The basic types of data for the site characterization are summarized in Table 3-2.

When data to characterize the site are limited or unavailable, it is advisable to use information from analog sites as discussed below.

Analog Sites for Vadose Zone Characterization*

Natural analogs refer to natural or anthropogenic (human-produced) systems in which processes similar to those expected to occur at a contaminant site have occurred over long time periods and large spatial scales. Analogs provide an important dimension to the understanding of flow and transport processes. For some systems, natural analogs are the only means of providing the necessary understanding of long-term (thousands of years) and large-scale (kilometers) behavior, which is required to provide the scientific confidence in models used for site characterization and performance assessment. Because analog sites demonstrate the development of natural processes over long time periods, they provide data that cannot be obtained otherwise, or data that are collected more easily and cost-effectively than by means of direct site

*This section was contributed by A. Simmons and M. Bandurraga, Lawrence Berkeley National Laboratory.

TABLE 3-2

Types of Investigations and Basic Types of Data for Site Characterization
(adapted from ASMT D 5979 - 96).

Types of Investigations	Types of Data
Topography and Remote Sensing	<ul style="list-style-type: none"> (a) Topography (b) Aerial photography (c) Satellite imagery (d) Multispectral data (e) Thermal imagery (f) Radar, side-looking airborne radar, microwave imagery
Geomorphology	<ul style="list-style-type: none"> (a) Surficial Surface geology or geomorphology maps (b) Engineering geology maps (c) Surface-water inventory maps (d) Hydrography digital line graphs
Geology	<ul style="list-style-type: none"> (a) Geologic maps and cross sections (b) Lithologic and drillers logs
Geophysics	<ul style="list-style-type: none"> (a) Gravity, electromagnetic forces, resistivity, and seismic survey data and/or interpretations (b) Natural seismic activity data (c) Borehole geophysical data
Climate	<ul style="list-style-type: none"> (a) Precipitation data (b) Temperature, humidity, and wind data (c) Evaporation data (d) Effects of climate change on hydrologic system information
Vegetation	<ul style="list-style-type: none"> (a) Communities and/or species maps (b) Density map (c) Agricultural species, crop calendars, consumptive use data (d) Land use/land cover maps
Soils	<ul style="list-style-type: none"> (a) Soil surveys (b) Soil properties determined from field and laboratory analysis
Hydrogeology	<ul style="list-style-type: none"> (a) Potentiometric head data (b) Subsurface test information (c) Subsurface properties determined from laboratory analyses (d) Previous work regarding modeling studies, hydrogeologic and groundwater system maps

continued

TABLE 3-2

Types of Investigations and Basic Types of Data for Site Characterization
(adapted from ASMT D 5979 - 96) (*continued*).

Types of Investigations	Types of Data
Hydrogeology (<i>cont.</i>)	<ul style="list-style-type: none"> (e) Spring and seep data (f) Surface water data (g) Well design, construction, and development information
Hydrochemistry/Geochemistry	<ul style="list-style-type: none"> (a) Subsurface chemistry derived from well samples (b) Surface water chemistry (c) Rock and soil chemistry (d) Water quality surveys
Anthropogenic Aspects	<ul style="list-style-type: none"> (a) Planimetric maps (b) Land use/land cover maps (c) Road, transportation, political boundary information (d) Land ownership maps, including historical information, if available (e) Resource management maps

characterization and monitoring. Because the analogs are observable, they also provide an important illustrative function of bolstering public confidence in at least some aspects of environmental restoration and waste disposal (Miller *et al.* 1994).

Analog sites must be carefully selected to exclude those for which initial conditions are poorly known and where important data, such as the source term, are poorly constrained. Chapter 13 of the Yucca Mountain Site Description Report (Rev.1, in press) describes the use of natural analog for applications in the Yucca Mountain Project, concerning the design to building confidence in understanding and modeling natural and engineered barrier system processes associated with the underground high-level nuclear waste disposal facility.

Using Data Quality Objectives in Designing Vadose Zone Monitoring Systems

Successful vadose zone characterization and monitoring programs must efficiently select and combine appropriate technologies to meet the program goals. In Chapter 2, these steps were defined in terms of managers and program directors “setting endpoints” and “developing a

roadmap.” Over the years, scientists and engineers have used various terms for these activities when applied to characterization and monitoring. Notably, recent literature describes these steps as the Data Quality Objective (DQO) Process. When performed correctly, the DQO process is a valuable tool in designing a program that provides maximum information for a reasonable cost. The DQO process is a mechanism for selecting and specifying consensus standards (for example, ASTM) and screening methods, where appropriate, and incorporating innovative technologies, where appropriate. The DQO process assists in defensibly selecting characterization and monitoring instrumentation, access needs, sample type(s), sampling frequency, and program duration. The DQO process considers technical needs and factors such as uncertainty and ultimate use of the information (for example, identifying critical exposure pathways, potential risks, and so forth).

It is critical that the DQO process is performed jointly by scientists, regulators, people with process and historical knowledge, and other potential technical contributors. The DQO process should be focused on defining a program built around a conceptual model and the stepwise refining of the conceptual model. Importantly, while the DQO process provides discipline and documentation, it should be implemented flexibly and creatively. As discussed below, to be successful, the process must maintain a focus on meeting the technical objectives and not be reduced to a process of defining success or quality by selecting only laboratory analyses from a list of regulatory numbered methods.

A detailed description of the DQO process is given in the case study on the accompanying CD, "The Use of Data Quality Objectives in Designing Vadose Zone Monitoring Systems," by Kevin Leary.

GENERAL APPROACH TO SELECTION OF SITE CHARACTERIZATION AND MONITORING METHODS

American Society for Testing and Materials (ASTM) Standards for Site Characterization and Monitoring

The subsurface conditions at a particular site are usually affected by a combination of a variety of natural factors and processes (such as geologic, tectonic, lithologic, topographic, geomorphologic, hydrologic,

water quality, hydrogeologic, geochemical, climatic, or microbiologic) and manmade factors and processes (such as waste disposal, contamination, or remediation). A rational site characterization program requires the application of a combination of complementary field, laboratory, and modeling methods to assess the impact of these influences. Consensus standards, such as those produced by ASTM, address both the general and specific procedures, as well as the types of data necessary to conduct qualitative conceptualization and quantitative site characterization and monitoring at any scale, including site-specific, subregional, and regional investigations.

When available, consensus standards are important and useful tools in developing a characterization and monitoring program. Thus, in the following discussion, we will identify ASTM standards related to different aspects of vadose zone characterization and monitoring.

ASTM standard D 5730-98 covers a general approach to improving the consistency of practice and planning a site characterization program for understanding environmental processes in soil and rock systems. This standard lists more than 400 field and laboratory test methods, practices, and guides, as well as a collection of non-ASTM references that describe field methods for site characterization and monitoring. Using this standard, it is possible to obtain an organized collection of information or a series of options for site characterization for environmental purposes. However, the standard does not recommend a specific course of action for each particular site, because ASTM standards cannot replace education and experience. The standard should instead be used in conjunction with professional judgment. Note that the word “standard” used in ASTM documents means that the document has been approved through the ASTM consensus process.

Table 3-3 provides a summary of field and laboratory methods for testing and analyzing soil, water, and waste samples collected during an environmental site investigation. This table also includes methods that are used routinely in field investigations to measure chemical parameters, as well as laboratory methods that are needed to obtain information relevant to the fate and transport of chemical and contaminant constituents in the subsurface.

TABLE 3-3**Summary of the Field and Laboratory Methods Pertinent to Environmental Site Characterization with References to the ASTM Standards**

(adapted from ASTM 5370-98 with modifications)

GENERAL

Reports	Indexing papers and reports (D 3584), use of modernized metric system (E 380)
Terminology	Soil, rock, and contained fluids (D 653); atmospheric sampling (D 1356); basic statistics (D 4743); waste and waste management (D 5681, D 5688 sampling and monitoring, D 5689 characterization); water (D 1189)
Objective-Oriented Guides	Acquisition of aerial photography and imagery for establishing historic site use and surficial surface conditions (D 5518)
<i>Contaminated Sites:</i>	Expedited site characterization (PS 85); developing conceptual site models for contaminated sites (E 1689); accelerated site characterization for petroleum releases (PS 3); risk-based corrective action at petroleum release sites (E 1739); short-term measures or early actions for site remediation (D 5745); environmental condition of property area types (D 5746); environmental baseline surveys (D 6008); real estate property transactions (E 1527, E 1528)
<i>Site-Characterization</i>	Environmental (D 5730, D 5995 cold regions; D 6067-ECPT); engineering and construction purposes (D 420)
<i>Septic System Characterization</i>	(D 5879); Subsurface (D 5921); sizing (D 5925)
<i>Environmental Management</i>	Development and implementation of a pollution prevention program (E 1609); lifecycle costing for pollution prevention (PS 14); assessment of buried steel tanks (ES 40); environmental regulatory compliance audits (PS 11); evaluation of an organization's environmental management system (PS 12); development and implementation of a source reduction program (PS 26)

SAMPLING

General	Collection and preservation of information and physical items by a technical investigator (E 1188); probability sampling of materials (E 105)
Air	Choosing locations and sampling methods for atmospheric deposition at nonurban locations (D 5111, D 5012); guide for laboratories (D 3614); flow rate calibration of personal sampling pumps (D 5337); planning ambient air sampling (D 1357); ambient air analyzer procedures (D 3249); sampling stationary source emissions (D 5835)

continued

TABLE 3-3

Summary of the Field and Laboratory Methods Pertinent to Environmental Site Characterization with References to the ASTM Standards (*continued*)
(adapted from ASTM 5370-98 with modifications)

<i>Airborne Microorganisms</i>	Sampling at municipal solid waste facilities (E 884)
<i>Sampling Organic Vapors/Toxic Vapors</i>	Charcoal tube absorption (D 3686); canister (D 5466); detector tubes (D 4490); length-of-stain dosimeter (D 4599)
<i>Particulate Matter Determination</i>	Filter absorbance method (D 1704, D 1704M); high-volume sampler (D 4096, D 4536); dustfall (D 1739-settleable particulates)
<i>Worker Protection</i>	Air monitoring at waste management facilities for worker protection (D 4844); air sampling strategies for worker and workplace protection (E 1370); collection of airborne particulate lead during abatement and construction activities (E 1553); activated charcoal samplers (D 4597), liquid sorbent diffusional samplers (D 4598); pesticides and PCBs (D 4861); Sampling indoor air quality of building (D 5791)
Biological Materials	Aseptic sampling (E 1287); see also Table A2 in ASTM D 5730-98
Soil/Rock/Sediments	Minimum set of data elements for soil sampling (D 5911)
<i>Drilling Methods</i>	Cable tool (D 5875); casting advancement (D 5872); diamond core drilling (D 2113); direct air rotary (D 5782); direct fluid rotary (D 5783); direct rotary wireline (D 5876); dual-wall reverse circulation (D 5781); hollow-stem auger (D 5784)
<i>Field Sampling and Handling Methods</i>	Auger sampling (D 1452); radionuclides (C 998); ring-lined barrel (D 3550); split barrel (D 1586); thin-wall tube (D 1587); volatile organics (D 4547)
<i>Sediments</i>	Sediments (D 4411-fluvial sediment in motion, D 4823-submerged, D 3213-handling, storing, and preparing soft undisturbed marine soil; E 1391-collection for toxicological testing)
Vadose Zone Water	
<i>Field Methods</i>	Pore liquids (D 4696); soil (D 4700); soil gas (D 5314); purgeable headspace sampling (D 3871); waterborne oils (D 4489); continual online monitoring (D 3864); filterable and nonfilterable matter (D 5907); online sampling/analysis (D 5540-flow and temperature control), water-formed deposits (D 887)
<i>Planning</i>	Water-quality measurement program (D 5612); water-monitoring programs (D 5851)
<i>Groundwater</i>	Sampling methods (D 4448); direct push sampling (D 6001); planning a ground-water sampling event (D 5903)

continued

TABLE 3-3

Summary of the Field and Laboratory Methods Pertinent to Environmental Site Characterization with References to the ASTM Standards (*continued*)
(adapted from ASTM 5370-98 with modifications)

<i>Surface Water</i>	Dipper or pond sampler (D 5358); closed conduits: equipment (D 1192); sampling (D 3370); laboratory practices: D 3856
Waste/Contaminants	
<i>General Guidance</i>	General planning (D 4687); representative sampling (D 6044); composite sampling and field subsampling (D 6051); heterogeneous wastes (D 5956)
<i>Specific Sampling Procedures</i>	Bituminous materials (D 140); ColiWasa (D 5495); drums general (D 6063 consolidated solids-D 5679, unconsolidated solids-D 5680); pipes and other point discharges (D 5013); scoop (D 5633); unconsolidated waste from truck (D 5658); UST release detection devices (E 1430, E1526); volatile organics (D 4547); waterborne oils (D 4489); oil/water mixtures for oil spill recovery equipment (F 1084); waste piles (D 6009)
Preservation/ Transport	
<i>Field Methods</i>	<p>Sample chain of custody (D 4840); estimation of holding time for water samples (D 4515, D4841)</p> <p>Rock core samples (D 5079); sample containers for organic constituents (D 3694); soil samples (D 4220); sediments for toxicological testing (E 1391); preservation/preparation of waterborne oil samples (D 3325, D 3326); handling, storing, and preparing soft, undisturbed marine soil (D 3213)</p> <p>Decontamination of field equipment, nonradioactive waste sites (D 5088); low-level radioactive waste sites (D 5608)</p>
Data Management/ Analysis	
<i>QA/QC</i>	Waste-management environmental data (D 5283); waste-management DQOs (D 5792); precision and bias (E 177); QC specification for organic constituents (D 5789)
<i>Data Analysis</i>	Evaluation of technical data (E 678); outlying observations (E 178); reporting results of examination and analysis of water-formed deposits (D 933)
<i>Geostatistics</i>	Reporting geostatistical site investigations (D 5549); analysis of spatial variation (D 5922); selection of kriging methods (D 5923); selection of simulation approaches (D 5924)
<i>Spatial Data</i>	Digital geospatial metadata (D 5714); see also Groundwater (Data Analysis)

continued

TABLE 3-3

Summary of the Field and Laboratory Methods Pertinent to Environmental Site Characterization with References to the ASTM Standards (continued)
(adapted from ASTM 5370-98 with modifications)

SOIL/ROCK HYDROLOGIC PROPERTIES

Infiltration Rate

<i>Field Methods</i>	Double-ring infiltrometer (D 3385); sealed double-ring infiltrometer (D 5093)
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Matric Potential

<i>Field Methods</i>	Tensiometers (D 3404)
<i>Laboratory Methods</i>	Filter paper method (D 5298)

Water Content

<i>Field Methods</i>	Calcium carbide method (D 4944); neutron probe (D 3017-shallow depth, D 5220-depth probe, D 6031-horizontal, slanted, and vertical access tubes)
<i>Laboratory Methods</i>	Direct heating method (D 4959); microwave oven method (D 4643); standard oven-drying method (D 2216); centrifuge moisture equivalent (D 425)

Hydraulic Conductivity

<i>Field Methods</i>	Vadose zone (D 5126)
<i>Laboratory Methods</i>	Granular soils (D 2434 - >1 3 10-3 cm/sec); low permeability soils (D 5084 - <1 3 10-3 cm/sec); rigid-wall compaction-mold permeameter (D 5856); effect of freeze/thaw (D 6035); peat (D 4511)

Other Hydrologic Properties

<i>Laboratory Methods</i>	Air permeability (D 4525); Soil water retention (D 2325-medium/coarse-textured, D 3152-fine-textured)
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SOIL/ROCK PHYSICAL PROPERTIES

Particle Size

<i>Soil Laboratory Methods</i>	Analysis (D 422); dry preparation (D 421); <200 sieve (D 1140); wet preparation (D 2217)
<i>Sediment</i>	Selection of methods for fluvial sediment (D 4822)

continued

TABLE 3-3

Summary of the Field and Laboratory Methods Pertinent to Environmental Site Characterization with References to the ASTM Standards (*continued*)
(adapted from ASTM 5370-98 with modifications)

Soil Density

Field Methods Drive cylinder (D 2937); gamma-gamma (D 2922 - <129, D5195 - >129); (D 4531); penetration (D 1586); rubber-balloon method (D 2167), sand-cone method (D 1556); sand replacement method (D 4914); selve method (D 4564); water-replacement method (D 5030); nuclear method (D 6031)

Pore Volume/Specific Density

Laboratory Methods Pore volume (D 4404); specific gravity (D 854, D 5550 - gas pycnometer)

Cone Penetration

Field Methods: In situ cone-penetration testing (D 3441, D 5778); CPT stress-wave energy measurements (D 4633); liquefaction potential evaluation (D 6066); ECPT for environmental site characterization (D 6067)

Classification

Field Methods: Field logging (D 5434); noncohesive sediments (D 5387); peat (D 4544-deposit thickness, degree of humification-D 5715); sediments (D 4410); visual-manual procedure (D 2488-unified, D 4083-frozen soils); rock mass classification (D 5878); rock quality designation (D 6032);

Laboratory Methods Dimension stone (C 199); frozen soils (D 4083); natural mineral aggregates (C 294); peat (D 2607); unified soil classification (D 2487)

Geophysical Properties

Field Methods Crosshole seismic testing (D 4428/D 4428M); seismic refraction (D 5777); soil resistivity (G 57 - Wenner 4-electrode method); planning and conducting borehole geophysical logging (D 5753)

Engineering Properties

In Situ Field Methods Bearing capacity/ratio (D 1194, D 4429); deformability and strength of weak rock (D 4555); direct shear strength (D 4554, D 5607); erodibility (D 5852), frost heave/thaw, susceptibility (D 5918); extensometers (D 4403); in situ creep (D 4553); in situ modulus of deformation (D 4394-rigid plate, D 4395-flexible plate, D 4506-radial jacking test, D 4729-flatjack method, D 4791-borehole jack); in situ stress (D 4623-borehole deformation gage, D 4645-hydraulic fracturing, D 4729-flatjack method); pressure measurement (D 4719-pressuremeter, D 5720-transducer calibration); vane shear test (D 2573)

continued

TABLE 3-3	Summary of the Field and Laboratory Methods Pertinent to Environmental Site Characterization with References to the ASTM Standards <i>(continued)</i> (adapted from ASTM 5370-98 with modifications)
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<i>Laboratory Methods</i>	California bearing ratio (D 1883); classification (D 2487); compaction (D 698, D 1557, D 5080); compressive strength (D 2166, D 2938); consolidation (D 2435); core dimensional and shape tolerances (D 4543); dispersive characteristics (D 4221-double hydrometer; D 4647-pinhole test); elastic properties (D 2845, D 3148); impact valve (D 5874); linear displacement (D 6027-calibrating transducers); liquid limit (D 4318); moisture content-penetration resistance (D 1558); one-dimensional swell (D 4546); plastic limit/plasticity index (D 4318); point load strength (D 5731); rock hardness (D 5873); shrinkage factors (D 427; D 4943); tensile strength (D 2936; D 3967); thermal properties (D 5334, D 5335); triaxial compression (D 2850, D 2664, D 4406, D 4767, D 5311, D 5407); uniaxial compression (D 4341, D 4405); use of significant digits (D 6026); vane shear test (D 4648);
Miscellaneous	
<i>Field Methods</i>	Geotechnical mapping of large underground openings in rock (D 4543)
<i>Laboratory Methods</i>	X-ray radiography (D 4452)
Peat/Organic Soils	
<i>Laboratory Methods</i>	Bulk density (D 4531); classification (D 2607); hydraulic conductivity (D 4511); pH (D 2976); moisture/ash/organic matter (D 2974)
Frozen Soils	
<i>Field Methods</i>	Description (D 4083)
<i>Laboratory Methods</i>	Creep properties by uniaxial compression (D 5520)

SOIL/ROCK CHEMISTRY

Basic Chemistry	
<i>Field Methods</i>	Soil pH for corrosion testing (G 51)
<i>Laboratory Methods</i>	Calcium carbonate (D 4373); pH (D 4972); soluble salt content (D 4542); diagnostic soil test for plant growth and food chain protection (D 5435); minimum requirements for laboratories engaged in chemical analysis (D 5522)
Soil Contaminants	
	Nitroaromatic and nitramine explosives (D 5143); screening fuels (D 5831); PCBs using room temperature phosphorescence (PS 47)
Sediments	
	Preparation for chemical analysis (D 3975, D 3976)

continued

TABLE 3-3

Summary of the Field and Laboratory Methods Pertinent to Environmental Site Characterization with References to the ASTM Standards (*continued*)
(adapted from ASTM 5370-98 with modifications)

Sorption/ Leachability

See fate-related procedures in Table A.1 of ASTM 5730-98

GROUNDWATER**Characterization/
Monitoring**

Assessing aquifer sensitivity and vulnerability (D 6030); conceptualization and characterization (D 5979); existing wells (D 5980); monitoring karst and fractured rock aquifers (D 5717); statistical approaches for groundwater detection monitoring programs (PS 64)

Data Elements*Field Methods*

Minimum set (D 5254); additional identification descriptors (D 5408); additional physical descriptors (D 5409); additional usage description (D 5410); selection of data elements (D 5474)

*Data Analysis/
Presentation*

Presentation of water level information (D 6000); chemical analysis: diagrams for single analyses (D 5738); trilinear diagrams (D 5754); diagrams based on data analytical calculations (D 5877); use of maps (D 6036)

Monitoring Wells*Field Methods*

Design/installation (D 5092); protection (D 5787); decommissioning (D 5299); casing (D 1785, F 480); grout (C 150-portland cement); water level measurement (D 4750); well development in granular aquifers (D 5521); well discharge (D 5716-circular orifice weir, D 5737-guide to methods); maintenance and rehabilitation (D 5978)

Aquifer Hydraulic Properties*Field Methods*

Packer tests (D 4630, D 4631); aquifer tests with control wells (D 4105, D 4106, D 5269, D 5270, D 5472, D 5473); D 5920 - anisotropic unconfined; D 6028; (leaky confining beds); slug tests (D 4044, D 4050, D 4104, D 5785, D 5881, D 5912); constant draw-down for flowing wells (D 5787, D 5855); constant rate pumping (D 6034); partially penetrating wells (D 5850); test selection (D 4043)

Modeling

Site-specific application (D 5447); comparing simulation to site-specific information (D 5490); documenting model application (D 5718); defining boundary conditions (D 5609); defining initial conditions (D 5610); conducting sensitivity analysis (D 5611); simulation of subsurface air flow (D 5719); subsurface flow and transport modeling (D 5880) model calibration (D 5981); developing and evaluating codes (D 6025); describing functionality (D 6033)

continued

TABLE 3-3	Summary of the Field and Laboratory Methods Pertinent to Environmental Site Characterization with References to the ASTM Standards <i>(continued)</i> (adapted from ASTM 5370-98 with modifications)
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Chemistry

<i>Field Methods</i>	Acidity/alkalinity (D 1067); electrical conductivity/resistivity (D 1125); ion-selective electrodes (D 4127); low-level dissolved oxygen (D 5462); odor (D 1292); pH (D 1293, D 5464); redox potential (D 1498); test kits for inorganic constituents (D 5463); turbidity (D 1889); Extraction Methods: purgeable organics using headspace sampling (D 3871); micro-extraction for volatiles and semivolatiles (D 5241)
<i>Laboratory Methods</i>	Organic carbon (D 2579; D 4129; D 5173; D 6317); minimum requirements for laboratories engaged in chemical analysis (D 5522); see ASTM Volumes 11.01 and 11.02 generally

Microbiology

ATP content (D 4012); iron bacteria (D 932); sulfate-reducing bacteria (D 4412); microbial respiration (D 4478); microscopy (D 4454-total respiring bacteria, D 4455-epifluorescence); plating methods (D 5465); onsite screening heterotrophic bacteria (F 488)

SURFACE WATER

**Geometry/
Flow Measurement**

Depth measurement (D 5073, D 5909-horizontal positioning); measurement of morphologic characteristics of surface water bodies (D 4581); operating a gaging station (D 5674)

Discharge Step backwater method (D 5388)

Open Channel Flow Selection of weirs and flumes (D 5640); acoustic methods (D 4408); acoustic velocity method (D 5389); broad-crested weirs (D 5614); culverts (D 5243); developing a stage-discharge relation (D 5541); dye tracers (D 5613); electromagnetic current meters (D 5089); Palmer-Bowles flume (D 5390); Parshall flume (D 1941); rotating element current meters (D 4409); slope-area method (D 5130); thin-plate weirs (D 5242); velocity-area method (D 3858); width contractions (D 5129)

Open Water Bodies Water-level measurement (D 5413)

Other Characteristics

Suspended sediment concentration (D 3977); environmental conditions relevant to spill control systems (F 625)

Chemistry See Groundwater above

continued

TABLE 3-3

Summary of the Field and Laboratory Methods Pertinent to Environmental Site Characterization with References to the ASTM Standards (*continued*)
(adapted from ASTM 5370-98 with modifications)

WASTE / CONTAMINANTS

Waste Properties

<i>Field/Screening Methods</i>	Compatibility (D 5059); cyanides (D 5049); flammability potential (D 4982); oxidizers (D 4981); pH (D 4980); physical-description screening analysis (D 4979); radioactivity (D 5928); sulfides (D 4978); waste specific gravity/bulk density (D 5057)
<i>Laboratory Methods</i>	Waste bulk density (E 1109); biological clogging of geotextiles (D 1987); coal fly ash (D 5759); solid waste freeze-thaw resistance (D 4842); stability and miscibility (D 5232); wetting and drying (D 4843)
<i>Extraction Methods</i>	Single batch extraction methods (D 5233); sequential batch extraction with water (D 4793- water, D 5284-acidic extraction fluid); soxhlet extraction (D 5369); total solvent extractable content (D 5368); solvent extraction of total petroleum hydrocarbons (D 5765); shake extraction of solid waste and water (D 3987)
<i>Contaminant Fate</i>	See fate-related procedures in Table A.2 of ASTM 5730-98

Radioactive Materials

<i>Monitoring</i>	Detector calibration (E 181); radiation measurement/dosimetry (E 170); radiation protection programs for decommissioning operations (E 1167)
<i>Sampling/ Preparation</i>	Sampling surface soil for radionuclides (C 998); soil sample preparation for determination of radionuclides (C 999)

Asbestos

Screen analysis (D 2947)

OTHER SITE CONDITIONS

Field Atmospheric Conditions

Atmospheric pressure (D 3631); conversion unit and factors (D 1914); determining comparability of meteorological measurements (D 4430); humidity: dew-point hygrometer (D 4030); psychrometer (E 337); terminology (D 4023)

Wind

Anemometers (D 4480, D 5096, D 5741); surface wind by acoustic means (D 5527); wind vane (D 5741, performance -D 5366); see Volume 11.03 generally

Solar Insolation

Pyranometers (E 824, E 913, E 941); pyrheliometers (E 816)

Characterization and Monitoring Technologies at DOE Sites*

It is instructive to summarize characterization and monitoring technologies that have been used at Department of Energy (DOE) sites. Table 3-4 presents a summary of current technologies that have been used at Idaho National Engineering and Environmental Laboratory (INEEL), Oak Ridge National Laboratory (ORNL), and Savannah River Site (SRS) for site characterization and monitoring. This table is based on the eight survey responses that were obtained by Loaiciga, *et al.* (1997). These site-characterization technologies are mostly conventional rather than innovative. Innovative technologies for soil and groundwater sampling and probing, such as the Geoprobe push-down sampler and the Site Characterization and Analysis Penetrometer System (SCAPS), were not reported in use at INEEL, while both are used at SRS. Geoprobe is only used at ORNL. INEEL personnel explained during the survey that site characterization is currently performed in a definitive-level mode rather than in a screening-level mode. This poses restrictions on the type of technologies that can be deployed *in situ*, according to regulator-approved standard operating procedures, to collect and analyze data used in risk analysis decisions.

According to Table 3-4, only a few vadose zone water and gas monitoring technologies were used. Only conventional suction lysimeters were in use at all three sites. Evidently, vadose zone sampling for air and water relies heavily on traditional soil coring devices, such as the split-spoon sampler to retrieve soil samples, which are then shipped to a laboratory for full analytical characterization.

Remote sensing is applied at all three sites primarily for topographic mapping and surface environmental reconnaissance of temperature, vegetative status, and gamma activity, as seen in Table 3-4. Remote sensing mapping allows fast, regional-scale assessment of surface properties, typically conducted on a preliminary screening level.

It is also evident from Table 3-4 that numerical models showed strong acceptance and a wide range of applications at all three sites. The main reason is that environmental restoration has progressed from screening- and definitive-level characterization to risk analysis, cleanup, contain-

*This section was contributed by H. Loaiciga, S. Renehan, and S. Weeks.

ment, and remediation. As a result, models have become useful tools for creating and analyzing a variety of scenarios in a very cost-effective manner. For example, a mass transport numerical model can simulate the fate and transport of a contaminant (such as benzene) in groundwater that is being pumped, treated, and recharged according to a specific pump-and-treat scheme. A vadose zone model such as SESOIL (Seasonal Soil Compartment Model, Bonazountas and Wagner 1984) may be implemented to assess the effect of soil capping on long-term metal vertical migration in the vadose zone. Modelers typically are part of the risk-analysis group at the surveyed sites.

One aspect of site characterization that was overlooked initially by the survey relates to ecological monitoring. ORNL and SRS maintain active monitoring of vegetation, fish, mammals, and other species, as well as of surface-water bodies. Living organisms are tested primarily for radionuclides and metals (such as cesium and strontium isotopes, and mercury) that accumulate in their tissues. Ecological monitoring is done by capturing and/or sampling of specimens and testing parts or tissue in the laboratory according to standard protocols.

TABLE 3-4

Summary of Current Site Characterization and Monitoring Technologies Used at INEEL, ORNL, and SRS.

Technology	INEEL	ORNL	SRS
<i>Remote Sensing</i>			
Remote sensing/aerial photography	+	+	+
<i>Surface Geophysics</i>			
Electrical resistivity	+	+	+
Electromagnetic conductivity	+	+	+
Seismic methods	Past use	+	+
Ground-penetrating radar	+	+	+
Magnetometer surveys		+	+
<i>Borehole Geophysics</i>			
Resistivity surveys	+	+	+
Cross-borehole tomography	+		+

continued

TABLE 3-4

Summary of Current Site Characterization and Monitoring Technologies Used at INEEL, ORNL, and SRS. *(continued)*

Technology	INEEL	ORNL	SRS
<i>Nuclear Logging</i>			
Density logging	+	+	+
Nuclear logging (natural gamma, neutron logging, gamma-gamma radiation)	+	+	+
<i>Drilling</i>			
Geoprobe®-type penetrometer		+	+
Large site characterization and analysis penetrometer system (SCAPS) platform			+
Standard methods (hollow-stem auger, rotary, and so on)	+	+	+
Direct sonic drilling	Past use		+
Rotosonic drilling	Past use	+	+
Horizontal drilling	Past use	+	+
<i>Groundwater Sampling</i>			
Sampling (bladder, dedicated pumps, and so on)	+	+	+
Sampling bailers (such as thief sampler)	+	+	+
<i>Soils Characterization</i>			
Sampling technologies (discrete, continuous, and so on)	+	+	+
<i>Vadose Zone Water and Gas Monitoring</i>			
Lysimeter (suction, pressure/vacuum, and so on)	+	+	+
Electrical resistivity blocks	Past use		
Soil-gas monitoring (probes, chambers, and so on)	+		+

TABLE 3-4**Summary of Current Site Characterization and Monitoring Technologies Used at INEEL, ORNL, and SRS. (continued)**

Technology	INEEL	ORNL	SRS
Time domain reflectometry	+		
Electronic leak detection system			
Thermocouple psychrometers			
Tensiometers	Past use		+
Frequency domain capacity probes			
Automatic VOC collection/gas chromatography			
Analytical Technologies			
Gas chromatography	+	+	+
High-performance liquid chromatography			+
Thin-layer chromatography			
Super-critical fluid chromatography			
Gas chromatography/mass spectrometry	+	+	+
Mass spectrometry	Past use	+	+
Ion-mobility spectrometry			
Atomic-absorption spectrometry	Past use	+	+
Atomic-emission spectrometry		+	+
Laser-induced breakdown spectrometry			
Infrared spectrometry (Fourier transform, and so on)	Past use	+	+
Near IR reflectance/transmission spectrometry			
Raman spectroscopy			
UV-visible spectrometry (fluorescence, synchronous luminescence, etc.)		+	+
Fluorescence spectrometry	+		+
X-ray fluorescence	Past use		+
Gamma spectrometry	+		+
Radiation detectors (Geiger counter, solid/liquid scintillator, semi-conductor detector, and so on)	+	+	+

continued

TABLE 3-4 **Summary of Current Site Characterization and Monitoring Technologies Used at INEEL, ORNL, and SRS. *(continued)***

Technology	INEEL	ORNL	SRS
Nuclear magnetic resonance			+
Photo-ionization detector	+	+	+
Electrical conductivity sensor		+	+
Electrochemical techniques			+
Explosive sensor			+
Free product sensor			+
Fiber optics sensor (solid, porous, etc.)			+
Piezoelectric sensors			+
In situ chemical probes (chlorine, pH/ORP, TDS, DO, and so on)	+	+	+
Membrane-based testing devices (RDX, TNT, PCBs, and so on)		+	+
Environmental test kits (color testing, titrimetric testing, immunassays)	+	+	+
Detector tubes	+		+
<i>Numerical/Spatial/Statistical Models</i>			
Geostatistical/statistical	+	+	+
Flow and transport models	+	+	+
Geographic/expert/decision support systems	+	+	+

Legend:
A plus sign in Table 3-4 means that the technology is currently used.
A blank space in the table indicates neither current nor past use of a specific technology.

SELECTION OF DRILLING AND SOIL SAMPLING METHODS*

Drilling

Selection of an appropriate drilling method is the primary step in site characterization and monitoring (Driscoll, 1986; Nielsen and Schalla, 1991). The decision should be based on the specific characteristics of each site, including, but not limited to, the geologic, hydrogeologic, topographic, climatic, and anthropogenic conditions of the site. Selection of a drilling method must also consider the goal of the drilling (for instance, soil and fluid sampling requirements, and/or monitoring equipment installation). Further, horizontal drilling and boring machines are emerging as useful adjuncts to vertical drilling for environmental work, especially methods minimizing the use of drilling fluids.

The ASTM D 6286-98 Standard Guide for Selection of Drilling Methods for Environmental Site Characterization summarizes most drilling methods available (Table 3-5), and provides the advantages and disadvantages of each method. The two main classes of drilling methods are auger drilling and fluid-rotary drilling. Other, less common methods are vibratory drilling, cable-tool drilling, and jet drilling. Casing-drive systems, which are typically combined with fluid-rotary, cable-tool, or jet drilling techniques, provide another drilling method. Vibratory drilling is best understood as a type of highly efficient casing-drive system. Casing-drive systems are less commonly used alone for borehole drilling. Direct-push methods, such as the cone penetrometer (CPT), are discussed in the section “Cone Penetrometer and Direct Push Tools for Vadose Zone Characterization,” below.

Of the drilling methods listed in Table 3-5, water-based fluid-rotary methods and jet-drilling methods can introduce large quantities of water to the subsurface. This result may be unacceptable, because the water will disturb all of the parameters of interest, including saturation, permeability, microbial community structure, and the concentrations and distributions of the chemical constituents. Therefore, water-based fluid-rotary methods and jet-drilling methods generally should not be used for vadose zone investigation.

*This section was contributed by B. Faybishenko and P. Jordan.

TABLE 3-5 Summary of well Well-Drilling Methods (ASTM 6286-98)

Drilling Method	Drilling Fluid	Casing Advance	Type of Material Drilled	Typical Drilling Depth, in ft^A.	Typical Range of Borehole Sizes, in In.	Samples Obtainable^B	Coring Possible
Power auger (Hollow-stem)	none, water, mud	yes	soil, weathered rock	<150	5-22	S, F	yes
Power auger (Solid-stem)	water, mud	no	soil, weathered rock	<150	2-10	S	yes
Power bucket auger	none, water (below water table)	no	soil, weathered rock	<150	18-48	S	yes
Hand auger	none	no	soil	<70 (above water table only)	2-6	S	yes
Direct fluid rotary	water, mud	yes	Soil, rock	>1000	2-36	S, R	yes
Direct air rotary	air, water, foam	yes	soil, rock	>1500	2-36	S, R, F	yes
DTH hammer	air, water, foam	yes	rock, boulders	<2000	4-16	R	yes
Wireline	air, water, foam	yes	soil, rock	>1000	3-6	S, R, F	yes
Reverse fluid rotary	water, mud	yes	soil, rock	<2000	12-36	S, R, F	yes
Reverse air rotary	air, water, foam	yes	soil, rock	>1000	12-36	S, R, F	yes
Cable tool	water	yes	soil, rock	<5000	4-24	S, R, F (F-below water table)	yes
Casing-advancer	air, water, mud	yes	soil, rock, boulders	<2000	2-16	S, R, F	yes
Direct-push technology	none	yes	soil	<100	1.5-3	S, F	yes
Sonic (vibratory)	none, water, mud, air	yes	soil, rock, boulders	<500	4-12	S, R, F	yes
Jet percussion	water	no	soil	<50	2-4	S	no
Jetting	water	yes	soil	<50	4	S	no

^AActual achievable drilled depths will vary depending on the ambient geohydrologic conditions existing at the site and size of drilling equipment used. For example, large, high-torque rigs can drill to greater depths than their smaller counterparts under favorable site conditions. Boreholes drilled using air/air foam can reach greater depths more efficiently using two-stage positive-displacement compressors having the capability of developing working pressures of 250 to 350 psi and 500 to 750 cfm, particularly when submergence requires higher pressures. The smaller rotary-type compressors only are capable of producing a maximum working pressure of 125 psi and produce 500 to 1200 cfm. Likewise, the rig mast must be constructed to safely carry the anticipated working loads expected. To allow for contingencies, it is recommended that the rated capacity of the mast be at least twice the anticipated weight load or normal pulling load.

^BSoil = S (Cuttings), Rock = R (Cuttings), Fluid = F (some samples might require accessory sampling devices to obtain).

Soil Sampling

Soil samples from the vadose zone are collected during drilling and are to be used for various aspects of site characterization, including stratigraphic description, measurements of moisture content and matric potential, testing of hydraulic conductivity and water retention, geotechnical testing, soil-gas analyses, microbiological investigations, and chemical analyses of pore liquid and soils (ASTM 4700-91). Soil samples are also used for chemical analyses of liquids, solids, and gases to determine the presence, possible source, migration route, and physical-chemical behavior of contaminants in the vadose zone.

Two types of vadose zone sampling devices have been designed: (1) samplers used in conjunction with hand-operated devices, and (2) samplers used in conjunction with multipurpose or auger drill rigs. These devices are included in the ASTM Guide 4700-91. During drilling, encased and uncased soil samples can be taken from specific depths according to requirements of the analyses.

A major disadvantage of hand-operating samplers (such as screw-type augers, barrel augers, tube-type samplers, and hand-held power augers) is the limited depth of sampling. Sampling devices used in conjunction with hollow-stem augers and in holes advanced by solid-stem augers include thin-walled tube samplers (also called Shelby tubes), split-barrel drive samplers (also called split spoons), ring-lined barrel samplers, continuous-sample tube systems, and piston samplers. These samplers are either pushed (or driven) in sequence with an increment of drilling, or are advanced simultaneously with the progression of a hollow-stem auger column. It is necessary to take into account that, in general, the soil-sampling methods are destructive, and multiple sampling at the same location is not possible. During drilling, sampling, and sample preparation for the analysis, some portions of soil gas and liquid are usually lost, which may lead to erroneous results, as shown in the case study “Comparison of Vadose Zone Soil and Water Analytical Data for Characterization of Explosives Contamination.”

The case study, “Comparison of Vadose Zone Soil and Water Analytical Data for Characterization of Explosives Contamination,” by Wilson S. Clayton, Ph.D., P.G., and Peter Wirth, P.E., compares the analytical results obtained from soil samples with those acquired from permanently installed suction lysimeters. *See page 423.*



Disturbed soil samples obtained by backhoe, bucket auger, or other destructive techniques may lose volatile components during soil sampling. Special procedures to restrain biodegradation of VOCs using methanol, and solution of cupric sulfate, are described in the ASTM Standard D 4547-98, "Sampling Waste and Soils for Volatile Organic Compounds."

The reliability of the sampling procedure for site characterization can be significantly increased using an innovative adaptive-sampling approach, which is described in the case study on the accompanying CD, "Adaptive Sampling Approach to Environmental Site Characterization," by Grace Bujewski, Sandia National Laboratories. This approach was used for soil sampling to detect radiation, organic compounds, and metals, and showed a significant cost saving compared to the conventional RCRA site characterization.



CONE PENETROMETER AND DIRECT PUSH TOOLS FOR VADOSE ZONE CHARACTERIZATION*

Over the past twenty years, one of the most important technological developments for vadose zone characterization of unconsolidated sediments is the direct-push method for accessing and probing the subsurface. The cone penetrometer and related direct-push technologies, such as the Geoprobe®, have been increasingly used for geologic and chemical characterization at sites throughout the United States and elsewhere. In addition to the standard suite of sensors (that is, tip pressure, sleeve friction, and capillary pressure), the cone penetrometer has been used with innovative sensors and samplers to perform contaminated-site assessments, and has also been used to install wells. By integrating geologic information from the standard cone-penetrometer sensor with the depth-discrete chemical and physical information obtained from cone-penetrometer-based samplers and sensors, we can perform an accurate, rapid, and cost-effective characterization. Using the added capability of cone-penetrometer-installed wells, the placement of

*This section was contributed by J. Rossabi.

targeted remediation systems can be initiated during the characterization. Cone-penetrometer tests (CPT) provide high-resolution, high-quality data, are minimally invasive, and produce a minimum of investigation-derived waste. These attributes are critical to investigative and cleanup operations at large hazardous waste sites with heterogeneous sediments.

Background

Most environmental professionals would prefer to use noninvasive techniques for characterizing the subsurface. However, although promising surface geophysical methods are being developed, subsurface characterization at the resolution needed for most environmental site assessment currently requires accessing the subsurface. One of the least invasive ways of achieving subsurface access is to use the small-diameter (less than 5 cm) cone penetrometer. A cone-penetrometer test is performed by pushing an instrumented steel rod into the ground to determine the properties of the penetrated subsurface materials. The standard array of instruments on a cone penetrometer includes tip pressure, sleeve friction, and pore pressure sensors. This ensemble is commonly called a piezo-cone configuration. Geotechnical properties, stratigraphy, and soil type of the subsurface materials can be estimated using the data from these sensors (Lunne *et al.* 1997).

The cone penetrometer was first developed in the Netherlands in 1932 as a manually deployed instrument to determine hard soil zones and for measuring pile-bearing capacity, and has since developed into an automated system used throughout the world (Barentsen 1936). Currently the CPT is performed using a hydraulic pressure system to deploy the rods and a heavyweight truck to supply the inertial mass. Sensor data are collected and processed electronically with a typical resolution of approximately 2 cm. Depths of penetration vary, depending on the subsurface materials. For example, at the Savannah River Site (where there are coastal plain sediments), depths greater than 35 m are routine, with occasionally pushes beyond 85 m; however, refusal of penetration has also occurred at depths of less than 10 m (Rossabi *et al.* 1998). Conditions that cause refusal include the presence of gravel, cobbles, rock or highly consolidated-cemented strata. Sites with these attributes are less suited to CPT methods.

Predominately used for geotechnical applications such as bearing capacity and liquefaction, the CPT only recently has been used for environmental characterization. The fast and inexpensive access to the subsurface provided by the CPT makes it an ideal tool for contaminated-site investigations. In addition, the development of chemical and other sensors, combined with the geologic sensing of the CPT, has hastened the development of new protocols that substantially reduce characterization times and increase characterization accuracy.

The Department of Defense and Department of Energy have led the way in sponsoring the development, deployment, and testing of new sensors for the cone penetrometer. Significant developments and innovations in CPT technology have come from both government and private industry.

Direct Push Tools

As mentioned previously, the standard suite of devices on the cone penetrometer includes tip resistance, sleeve friction, and pore pressure sensors. This ensemble is commonly called a piezo-cone configuration. Electrical resistance measurement capability has been recently included as a standard tool in several cone penetrometers. (This measurement has a long history as a standard borehole-logging tool but only lately has been commonly implemented with the cone penetrometer.) In Figure 3-13, plots from the three standard cone penetrometer sensors (tip pressure, sleeve friction, and pore pressure) are displayed. Tip pressure or cone resistance is a measure of the normal force felt by the cone in a direction opposite to that of the push, approximately perpendicular to the ground surface. Sleeve friction is a measure of the frictional force on the outer cylindrical surface of the penetrometer rod related to the “stickiness” of the formation material. Pore pressure is a measure of the instantaneous pressure on the cone in a direction perpendicular to that of the push. In addition to these plots, the ratio of sleeve friction to tip pressure and electrical conductivity are plotted. The sleeve friction to tip pressure ratio is a useful construct for evaluating the behavior of the sediments. The electrical conductivity is generally measured directly through electrodes located on the outside of the cone and insulated from one another. Each of these measurements offers corroborating or complementary information about the penetrated sediments.

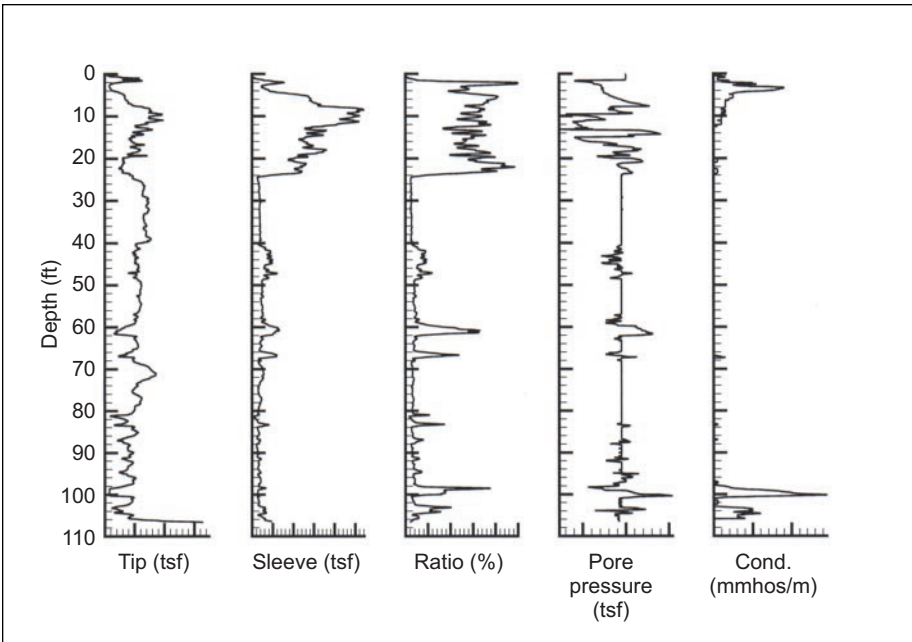


Figure 3-13. Cone penetrometer data from the vadose zone at the Savannah River Site

The sleeve-friction-to-tip-pressure ratio is often used as the most basic soil-behavior-type indicator (Lunne *et al.* 1997). From these data, the soil type can often be inferred (but not absolutely identified) according to grain-size distribution. In general, the lower the ratio, the higher the sand content of the soils, with a nominal value of 6 percent chosen as the demarcation line for clay. Unless a site-specific correlation is calculated, however, it is prudent to use the log in relative terms with a higher ratio corresponding to more clayey soils, and a lower ratio to sandier soils. Soil-behavior type is often defined using a more formal basis for soil-type classification, an empirically developed correlation chart based on tip pressure, friction ratio, and data from several sites (Douglas and Olsen 1981). Other soil classification methods have been developed from inclusion of the pore-pressure data with tip and sleeve information. Three examples of these charts are shown in Figure 3-14. The charts may have to be adjusted for more precise soil-behavior-type determination at specific sites, but they generally provide an accurate description of the subsurface materials.

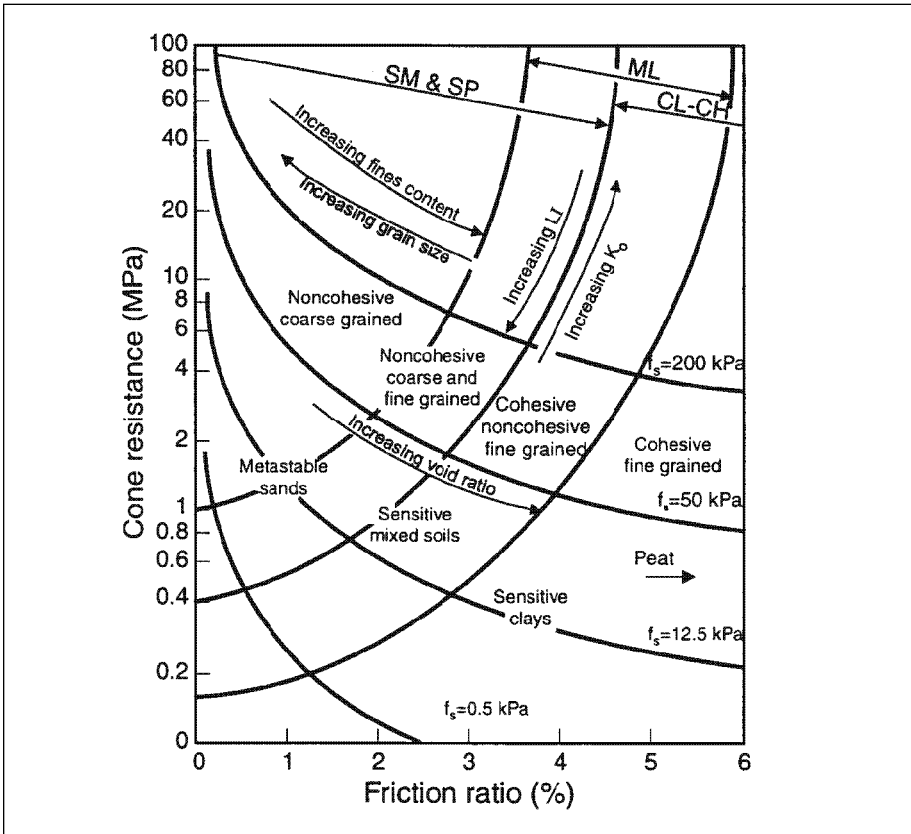


Figure 3-14. Three examples of empirically derived soil type classification charts
(continued)

The most compelling aspect of cone penetrometer data is its vertical resolution. The penetration rate for cone penetrometers is 2 cm/sec, and data acquisition systems accompanying these tools acquire data at a rate of approximately 1 Hz. The 2 cm resolution contrasts with conventional borehole logging tools with typical resolution of approximately 1 m. Even recovered core is rarely described at a resolution of less than 30 cm. The value of high-resolution data has been felt most strongly in the characterization of contaminated sites. Although subsurface data on the order of centimeters is rarely necessary for site structural assessments or production-well characterization, the flow and transport of subsurface contaminants is often strongly influenced by thin, discontin-

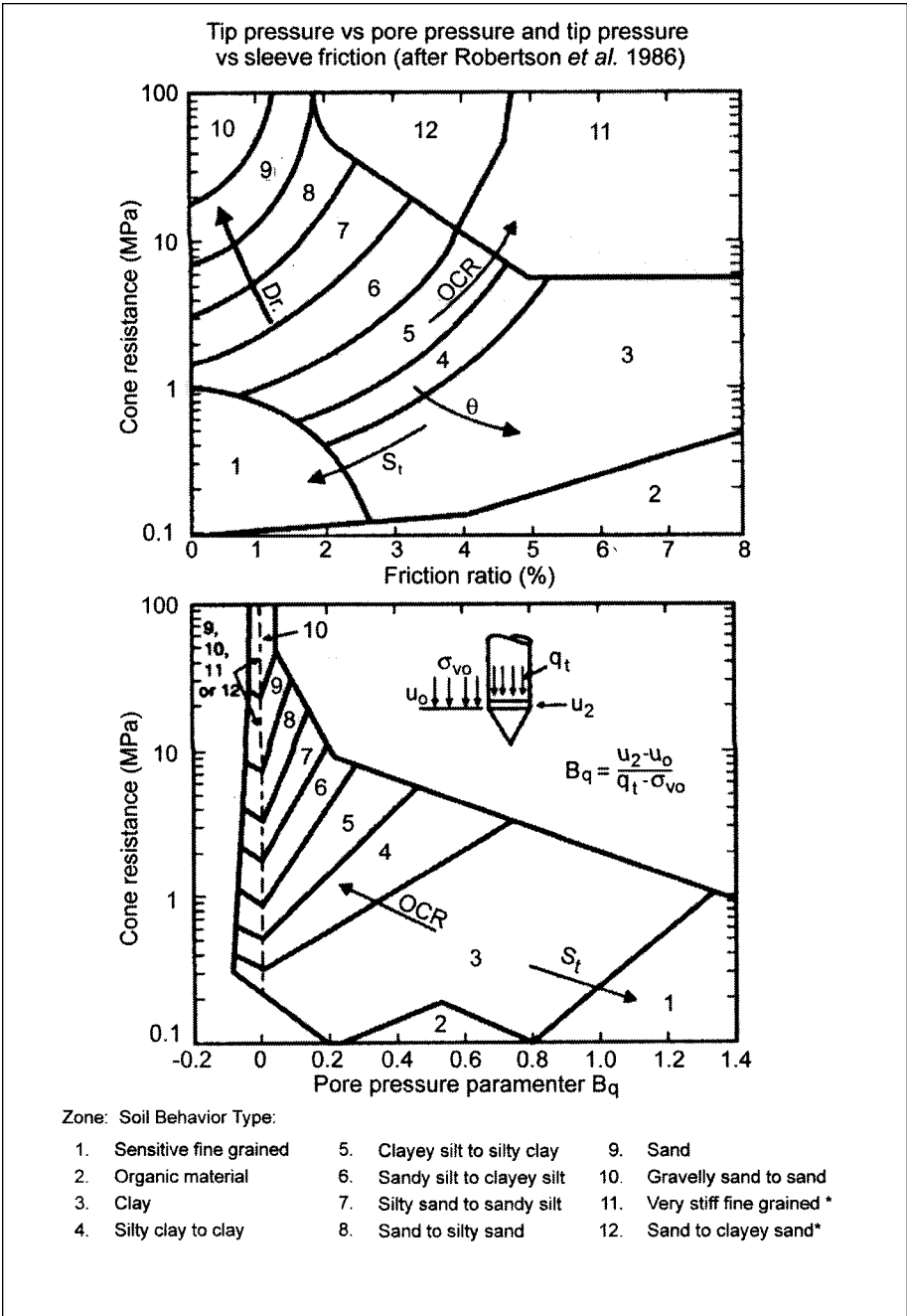


Figure 3-14. (continued)

uous layers. For example, a 2-cm layer of nearly saturated clay may prevent the downward migration of a nonaqueous phase fluid (NAPL). In addition, partially saturated materials with high capillary suction forces will absorb and retain nonaqueous phase fluids. Their slow dissolution into surrounding pore and infiltrating water permits the contaminants to act as a long-term source for years.

In Figure 3-13, the friction ratio indicates a clayey material from the ground surface to a depth of 24 ft below ground surface (bgs). The pore-pressure response corroborates these data. The electrical conductivity plot shows that the upper 12 ft of the clayey material is wet, with higher saturation values near the ground surface, as from a recent infiltration event. The plots show dry sand from 24 ft bgs to 60 ft bgs with a brief interval of fine sand or silt 41 to 49 ft bgs. Clayey layers are evident at 60, 68, and 83 ft bgs with very thin clayey laminates appearing between layers. The pore pressure sensor detects these laminates more clearly than the ratio log because the sleeve friction sensor (10 to 20 cm in length) tends to smear the ratio data resolution. The clay at 99 ft marks the beginning of an interbedded sand and wet clayey zone that continues until the saturated zone at a depth of 130 ft bgs.

These data collected at a site contaminated by volatile organic compound (VOC) releases near the surface have been important for targeting contaminant investigations. Figure 3-15 shows the friction ratio plot of Figure 3-13, as well as the plot of results of tetrachloroethylene (PCE) analyses performed on soil samples taken from two cores located near the cone penetrometer push. In this case, soil sampling was performed at the deeper, clayey zones, rather than at prescribed intervals, in order to minimize the chances of missing contamination and to reduce the expense of collecting and analyzing non-detects. Soil-gas sampling performed in this area identified high gas concentrations just above the 99-ft clay. It is clear from this plot that high residual concentrations of PCE are associated with the clayey zone. Further characterization activities near the release area would logically focus on the clay. For example, the cone penetrometer might be used to determine the topographic gradient of the 99-ft clay and track the migration of a dense nonaqueous phase liquid (DNAPL) source down the gradient surface.

One of the most important characteristics of the vadose zone is the amount of water in the predominately two-fluid phase system. The pore water is crucial to many subsurface processes (such as chemical and

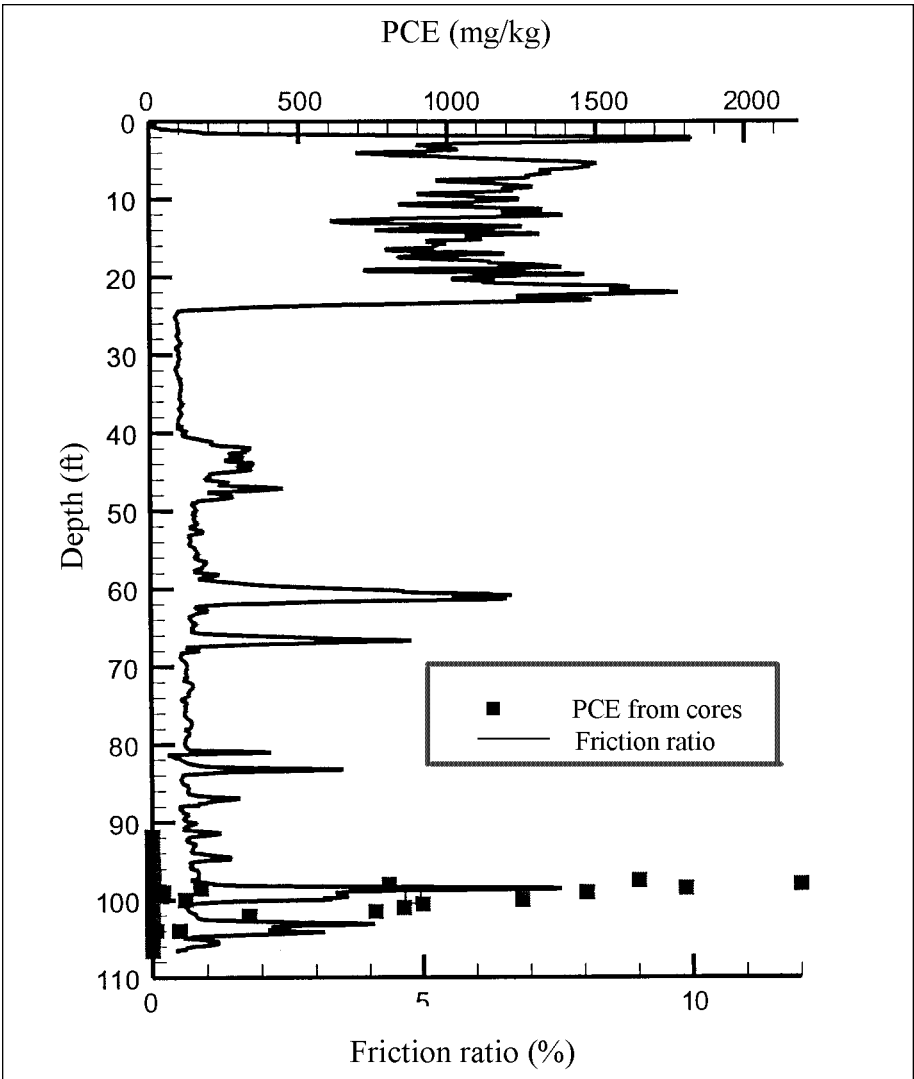


Figure 3-15. Comparison of friction ratio data with PCE concentration from soil cores

biological events), but it is especially important to the advective and diffusive transport of contaminants. The degree of saturation of subsurface sediments directly affects the relative permeability of potentially mobile fluids throughout the vadose zone. Accurate models of the subsurface for contaminant fate and transport rely on the intrinsic permeability values of individual strata within the model domain. These relatively time-


insensitive values provide the basis for determining the contaminant conductivity. The actual conductivity, however, is determined by the relative permeability of the contaminant fluid. This value depends on the presence and amount of other fluids in the system. For example, the transport of gases and nonaqueous phase liquids (NAPL) will be significantly reduced when they encounter a nearly water-saturated stratum of fine-grained sediments. A less water-saturated system will allow free transport of the gas, and, often, increased receptivity of the NAPL by imbibition through capillary suction. An important complication of the soil-moisture parameter is that it changes over time depending on the infiltration events to which the system is exposed. Therefore, knowledge of the soil moisture through time by multiple measurements or constant logging is desirable for the most accurate subsurface representation.

Several *in situ* methods of determining the soil-moisture characteristics of the unsaturated subsurface have been devised. The most commonly used methods are the *in situ* point techniques (such as the tensiometer and time domain reflectometer) and the borehole logging methods (neutron probes, for example). The point methods are reliable and accurate but can only provide information about the material immediately adjacent to the location of the fixed probe. The neutron log is valuable because it provides depth-discrete information over the full length of the borehole. The method has its drawbacks, however, in that it requires a radioactive neutron source, special well design and installation, and has a vertical resolution of approximately 30 cm or more. With lithology changes and associated water retention capacities that often occur at smaller scales than one foot, information impacting contaminant transport may be lost.

Recently, innovative tools for evaluating soil moisture have been developed for deployment with the cone penetrometer. These tools have many of the advantages of the *in situ* point measurement methods, but they are advanced through the depth of the vadose zone. They can therefore provide contiguous high-resolution measurements of the soil moisture properties of the vadose zone. Three commercially available probes for the CPT have been tested at the Savannah River Site. Two of the probes use a measurement of the dielectric properties of the subsurface in the frequency domain at a given point to determine the moisture content. The other, developed by Sandia National Laboratory personnel,


uses a time domain reflectometer in a cone section. All three methods provided very accurate results when compared to the baseline results obtained from Shelby tube samples and laboratory analysis.

“Case Study of Cone Penetrometer (CPT)-Based Soil Moisture Probes,”
by Joe Rossabi, describes the application of a cone penetrometer to the
problem of measurements of moisture content in soils. *See page 428.*



Cone penetrometer data might be used for specification of boundary conditions and heterogeneity in models, and for targeting zones for installation of tensiometers, lysimeters, or other equipment for which operation depends on soil type. Essentially, the standard cone penetrometer provides data that can be used in the same way as core description data, that is, to identify stratigraphic intervals and geologic features that are contextually related to any specific subsurface investigation.

An application of cone penetrometers for DNAPL detection is examined in the
case study **“Cone Penetrometer-Based Raman Spectroscopy for
DNAPL Characterization in the Vadose Zone,”** by J. Rossabi, B.D. Riha,
C.A. Eddy-Dilek, A. Lustig, M. Carrabba, K. Hyde, and J. Belo. *See page 431.*



In many cases, boreholes can be grout-sealed upon removal of the rods, further reducing the chances of cross-contamination and exposure. Wells (currently up to 5 cm in diameter) can also be installed directly into the formation using direct-push methods. Another use of direct-push technologies is the injection of fluids for either reaction with contaminants or creation of fractures in low-permeability soils. Tools that have been implemented with the cone penetrometer at the Savannah River Site or other sites are listed in Table 3-6, along with their use, the type of data they produce, their features, and their commercial status. Although this list is not exhaustive (new sensors and techniques are constantly being developed), it does show the amount and variety of tools that are compatible with direct-push methods.

TABLE 3-6		Sampling and Deployment Capabilities.		
Tool	Use	Data/Output	Features	Status
SOLID, LIQUID AND GAS SAMPLING				
FLUTE Membrane Installation	Sampling, chemical (NAPL), installation	Recovered sample, visual indicator, ports pressure, and so on	Cheap, fast, simple	CA-P
MOSTAP Sampler	Sediment samples	Tube or split spoon samples	Targeted depth	CA-P
Cone Sipper	Multi-depth liquid and gas samples	Liquid or gas samples	Multiple samples on single push	CA-P
BAT	Liquid samples	Septum-sealed sample	Targeted depth	CA-P
Bailing in Rods	Liquid samples	Liquid samples	Targeted depth	CA-S
Multilevel Gas	Gas samples	Gas samples	Targeted depths	CA-P
Wireline Sampler	Multi-depth sediment samples/cutting tool	Soil samples	Multiple samples on single push	UD
Well Point Samplers-Frits	Shallow groundwater, gas	Liquid or gas samples	Targeted depths	CA-P
Well-Inside Rod	Small diameter wells	Liquid or gas samples	Direct contact with the formation	CA-S
Well-Outside Rod	2-in. diameter wells	Liquid or gas samples	Direct contact with the formation	CA-S
Lysimeter	Vadose zone soil pore water	Liquid samples	Direct contact with the formation	FT
ERT (Electrical Resistivity) Probes	3D resistivity field	Relative soil moisture in plane or volume	Plane or volumetric differencing information	CA-S
Soil Moisture Probes	Volumetric soil moisture—single depth	Quantitative dielectric-based soil moisture values	Installed at a single depth	FT
PHYSICAL SENSING CAPABILITIES				
Standard	Lithology, soil properties	Soil behavior type classification	High resolution	CA-S,P
Temperature Sensor	Temperature	Temperature	Identify anomalous temperature perturbations	CA-P

continued

TABLE 3-6 **Sampling and Deployment Capabilities.** *(continued)*

Tool	Use	Data/Output	Features	Status
Science and Engineering Associates (SEA) Cone Permeameter	Pneumatic relative permeability, hydraulic	Depth-discrete conductivity	Targeted depths permeability	CA-S
Soil Moisture TDR	Volumetric soil moisture log	Quantitative time domain reflectometry-based soil moisture values	High vertical resolution	CA-S
Fiber Optic Probe	Capillary pore pressure	Relative humidity	<i>in situ</i> measurement of soil properties	FT
Soil Moisture Dielectric	Volumetric soil moisture log	Quantitative dielectric-based soil moisture values	High vertical resolution	CA-S
POLO (Subsurface Position Locating System)	Subsurface position relative to entry point at surface	Incrementing three-dimensional data on distance from datum	Physical position	FT
GeoVis Video Microscope	Grain size distribution, soil type, fluid behavior, contaminant identification	High -resolution color video	Very high resolution	CA-S,P
Inclinometers	Boring deviation	Deflection from normal	Infers physical position	CA-S
Vibratory Cone and Resonant Sonic Cone	Liquefaction of soils	Liquefaction parameters	Structural parameters and increased depth capability	CA-S
Seismic Cone	Density change, soil type, liquefaction	Geophone data	Structural parameters, identifies units	CA-S
Index of Refraction	Fluid phase change	Change of fluid	Identifies sharp phase changes	CA-P
Hyperlog	Soil color, contaminants	Munsell color charts and three-wavelength fluorescence	Augments soil type classification, identify fluorescence contaminants	CA-S

continued

TABLE 3-6

Sampling and Deployment Capabilities (*continued*)

Tool	Use	Data/Output	Features	Status
CHEMICAL SENSING CAPABILITIES				
Raman Spectroscopy	Nonaqueous phase compound identification	Inelastic scattering spectrum of compounds	Uniquely identifies nonaqueous phase contaminants <i>in situ</i>	CA-S,P
LIF (Laser-Induced Fluorescence)	Locate fluorophores	Fluorescence spectrum of compounds	Identifies nonaqueous phase compounds <i>in situ</i>	CA-S
ROST™ (Rapid Optical Screening Tool)	Locate fluorophores	Time domain fluorescence spectrum of compounds	Identifies nonaqueous phase compounds <i>in situ</i>	CA-S,P
FFD	Locate fluorophores	Fluorescence intensity of compounds	Detects nonaqueous phase compounds <i>in situ</i>	CA-S,P
Laser-Induced Breakdown	Identify inorganic compounds	Emission spectroscopy of compounds	Detects some nonaqueous phase inorganic compounds	FT
Hydrosparge	<i>In situ</i> measurement of aqueous phase compounds	Headspace measurement of volatile and semivolatile compounds	<i>In situ</i> aqueous measurement	CA-S
<i>In Situ</i> Soil Sensor	<i>In situ</i> thermal desorption and analysis of VOCs/ SVOCs	Heated headspace from <i>in situ</i> soil sample	<i>In situ</i> soil sample measurement	CA-S
Gas Analyzers at the Surface (Includes Chromatographic, Solid State and Other Detection Methods)	Analyze gas sample stream during penetration	Gas phase analysis of volatile compounds	Measures at the surface in real time	CA-S,P
Other In-Cone Gas Analyzers (such as RCI 5000, PAWS)	VOC measurement in the gas phase	Gas phase analysis of volatile compounds	Measures at the surface or in cone	FT
X-ray Fluorescence	<i>In situ</i> detection of metals/rads	X-ray fluorescence spectrum	<i>In situ</i> detection of metals/rads also clay components (such as titanium)	FT
Gamma Spectroscopy	<i>In situ</i> detection of Cs-137 and other gamma-emitters	Gamma spectrum	<i>In situ</i> detection of gamma emitters	CA-S

continued

TABLE 3-6 Sampling and Deployment Capabilities (*continued*)

Tool	Use	Data/Output	Features	Status
MIP (Member Interface Probe)	Detection of aqueous and nonaqueous phase volatiles	Membrane mediated organics in gas phase	Multiple depths, source identifier	CA-S,P
PiX (Precision Injection/Extraction of Alcohols)	Identify DNAPL	Increase concentration in injected and recovered solvent	NAPL identifier, probes volume around cone	FT
Fiber Optic TCE	Gas phase TCE <i>in situ</i>	Reagent-based gas and aqueous sensor	Sensitive at maximum containment levels (MCLs) for drinking water	FT

Legend:

CA-PS—Commercially Available for Purchase or Service

FT—Field Tested

UD—Under Development

Advantages and Limitations of Direct Push Methods

The cone penetrometer has many advantages over conventional methods of accessing the subsurface. Some of these are listed below.

- Rapid penetration (the normal push rate is 2 cm/sec)
- Minimally invasive (the diameter of the cone penetrometer rod is normally 4.445 or 3.175 cm)
- Minimal investigation-derived waste (no drill cuttings or other potentially hazardous waste)
- Can acquire multiple data sets simultaneously (three to five different kinds of measurements, as well as sampling, can be performed on a single push)
- Produces data in real time
- High vertical resolution (data are taken at least every 2 cm, and sensors are designed to exploit this capability)

- Direct formation contact (particularly useful for electrical resistivity and spectroscopy)
- Cost-effective (multiple logs and formation samples can be obtained in a single push, and wells can be installed in a second push at less than one-third the cost of conventional drilling and logging)

It is important to keep in mind the following limitations of the cone penetrometer:

- Used only in unconsolidated sediments (limits the number of sites that are accessible)
- Depth limitations (limited push capacity and formation resistivity limit the total depth achievable by the cone penetrometer to between depths of 3 and 100 m [10 and 300 ft])
- Small diameter (limits the types of tools that may be deployed in the cone penetrometer and also the size of wells that can be installed)
- Skin effects (created by the displacement and compaction of soils during the cone-penetrometer push—generally not significant)
- Inferred measurements (not practical to use for obtaining continuous core, so most cone-penetrometer logs, like traditional borehole logs, are inferred measurements from properties of the formation)
- May not be acceptable for long-term monitoring.

The use of direct-push technologies for vadose zone site characterization can greatly enhance the quality of the investigation. Daily operating costs of the cone penetrometer are comparable to those of conventional drilling, but the speed of penetration, low associated waste, minimal invasiveness, and the ability to deploy *in situ* and downhole sensors make the direct-push methods more cost-effective in many cases. The best method of applying direct-push methods and tools depends on the needs and resources of the specific site, and the application of these procedures and instruments will often serve to complement conventional drilling and other site-assessment methods. As with other characterization techniques, the direct-push method should be incorpo-

rated in the environmental professional's toolbox and used when appropriate.

Sources on Direct Push Technology

In addition to the references cited, private companies offering cone-penetrator or direct-push services, direct-push tool and instrument developers and manufacturers, and government sources (Department of Defense, Department of Energy, Environmental Protection Agency, and Department of Transportation) can supply information on direct-push technology. There is also information available on the following Internet sites:

- Geoprobe Systems Inc. <http://geoprobesystems.com/>
- Applied Research Associates, Inc. <http://www.ara.com/>
- Gregg In Situ Inc. <http://www.greggdrilling.com/INSitu.html>
- Fugro Geosciences <http://www.geo.fugro.com/>
- Department of Energy CMST program <http://www.cmst.org/>
- Liquifaction, the Web Site for the CPT Industry <http://www.liquefaction.com/index.html>.

ENVIRONMENTAL MEASUREMENT-WHILE-DRILLING SYSTEM FOR REAL-TIME SCREENING OF CONTAMINANTS*

One of the disadvantages of current characterization technologies is the lack of reliable observations and measurements conducted during borehole drilling. This drawback is especially significant for contaminated sites, because the soil and rock conditions can be altered by drilling tools and atmospheric air and water. Information on environmental conditions and drill-bit location and temperature during drilling is required in many environmental restoration operations. An inexpensive data collection system for identifying and tracking contaminant

*This section is based on the case study "Environmental Measurement-While-Drilling (EMWD) System for Real-Time Screening of Contaminants," by Cecelia Williams, on the accompanying CD.

concentrations and monitoring drill-bit conditions is needed for many waste-site procedures.

The Environmental Measurement-While-Drilling (EMWD) system (Figure 3-16) represents an innovative blending of new and existing technology in order to obtain real-time data during drilling. The objective of this method is to distinguish contaminated from non-contaminated areas in real time while drilling at hazardous waste sites. In EMWD, downhole sensors are located behind the drill bit and are linked by a high-speed data transmission system to a computer at the surface. As drilling is conducted, data is collected on the nature and extent of contamination, enabling on-the-spot decisions regarding drilling and sampling strategies. The EMWD system has been adapted by the integration of a gamma ray spectrometer (GRS) in place of the original simple gamma radiation detector. The GRS consists of a sodium iodide-thallium activated crystal coupled to a photomultiplier tube (PMT). The GRS output feeds to a multichannel analyzer (MCA). The MCA data, as a 256-channel gamma spectrum (100 KeV-1.6 MeV), is transmitted to the surface via a signal-conditioning and transmitter board. The system

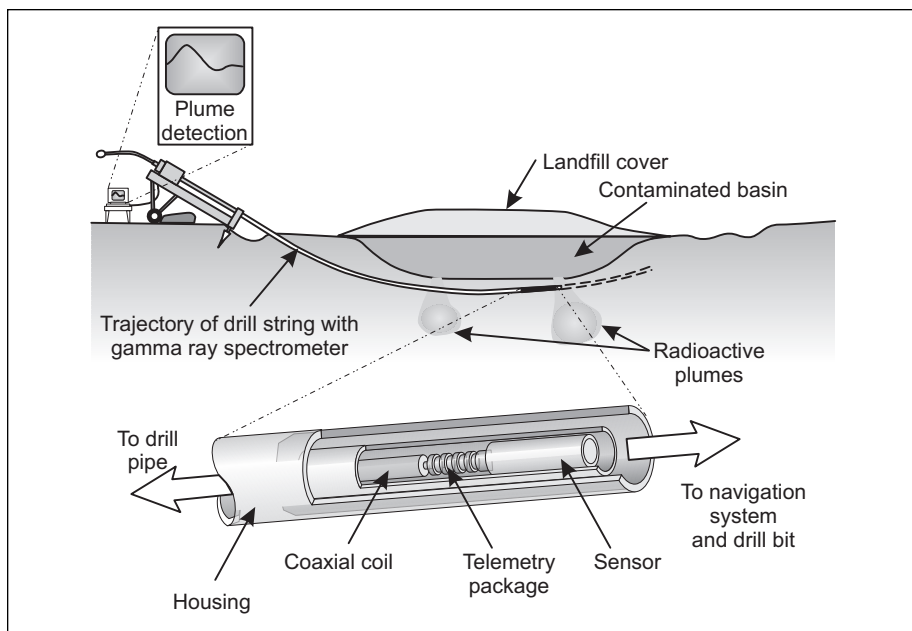


Figure 3-16. The Environmental Measurement-While-Drilling Tool.

also monitors the uphole battery voltage as measured downhole and the temperatures associated with the detector and instrumentation. The design includes data-assurance techniques to increase safety by reducing the probability of giving a “safe” indication when an unsafe condition exists.

The system provides real-time data on an eight differential/single analog multiplexer and any number of digital channels. Sampling speed from the analog channels can reach 100 kHz. The telemetry system is firmware-programmable to easily support many different data formats and additional data channels. The data transmission format (Digital FM Bi-phase, 4800 baud) provides excellent noise rejection for jumping the wireless connection between the rotating drill pipe and the stationary receiver. A Sandia-designed receiver removes the FM carrier, generates the data clock, and buffers data to be used by an IBM or IBM-compatible personal computer. A 28V rechargeable battery pack can supply downhole instrumentation power for more than 18 hours of drilling. The battery pack remains topside for easy maintenance and/or recharging.

The system is compatible with directional drilling techniques that use minimal drilling fluids and generate little-to-no secondary waste. The current system includes a continuous read-out-non-walk guidance and location system for use with the EMWD system. The orientation sensor package was integrated with the EMWD-GRS system without significant modification. In addition to the existing techniques, sensors are needed for the detection of heavy metals, volatile organic compounds, and natural gas. Technology developers are currently working with the EPA to obtain certification.

The EMWD system has many practical applications, including site characterization for contaminant detection and delineation. This system will guide sampling activities and borehole emplacement options. For example, a drill operator can back out of contaminated soils and redirect

The results of field testing of the EMWD are illustrated in the case study on the accompanying CD, “Environmental Measurement-While-Drilling (EMWD) System for Real-Time Screening of Contaminants,” by Cecelia Williams.



a drilling operation around the contamination. Other potential users of EMWD include utility emplacement and petroleum industries.

WELL COMPLETION AND INSTRUMENTATION

Permanent Well Completion

Wells drilled in hostile environments (such as weak, unconsolidated soils and sediments, fractured rocks, and contaminated sites) should be cased, and the annulus between the casing and the formation should be backfilled or grouted. Such procedures are intended to seal off unstable zones to prevent the collapse of the well, allow the installation of monitoring probes and periodic insertion of logging tools, and prevent cross-contamination of different layers along the borehole length.

Permanent well completion can be performed using borehole casings and backfilling the annulus. Steel or plastic casings, which usually span the entire length of the well, are often used to provide borehole wall stability (Rahman and Chilingarian 1995). Materials commonly used to seal the borehole annulus are bentonite, cement, or a mixture of both.

It is common practice to install an array of single monitoring probes in boreholes at different depths within fine-sand layers, separated by impermeable bentonite or cement. However, these materials may settle unevenly in the borehole, creating air pockets (Everett *et al.* 1984a,b). Water used to harden cement and swell bentonite pellets can be absorbed by the surrounding formation and thereby change the formation moisture content. If a water-conducting pathway intersects the sand layer in the borehole, water may accumulate in the sand layer around the monitoring probe or may perch on top of a bentonite seal (Figure 3-17). The presence of water may lead to erroneous measurements in boreholes. Moreover, field observations showed that the well-casing composition and bentonite may affect measurements conducted with logging tools and may contribute solutes to the groundwater (Houghton *et al.* 1984; Remenda and van der Kamp 1997).

During drilling at Hanford, it was assumed that the borehole annulus (the space between the soils and the casing) in unstable soils could remain ungrouted immediately after drilling, because the soils would ultimately collapse and seal the borehole annulus. However, observations at Hanford showed that the unstable soils did not seal off the

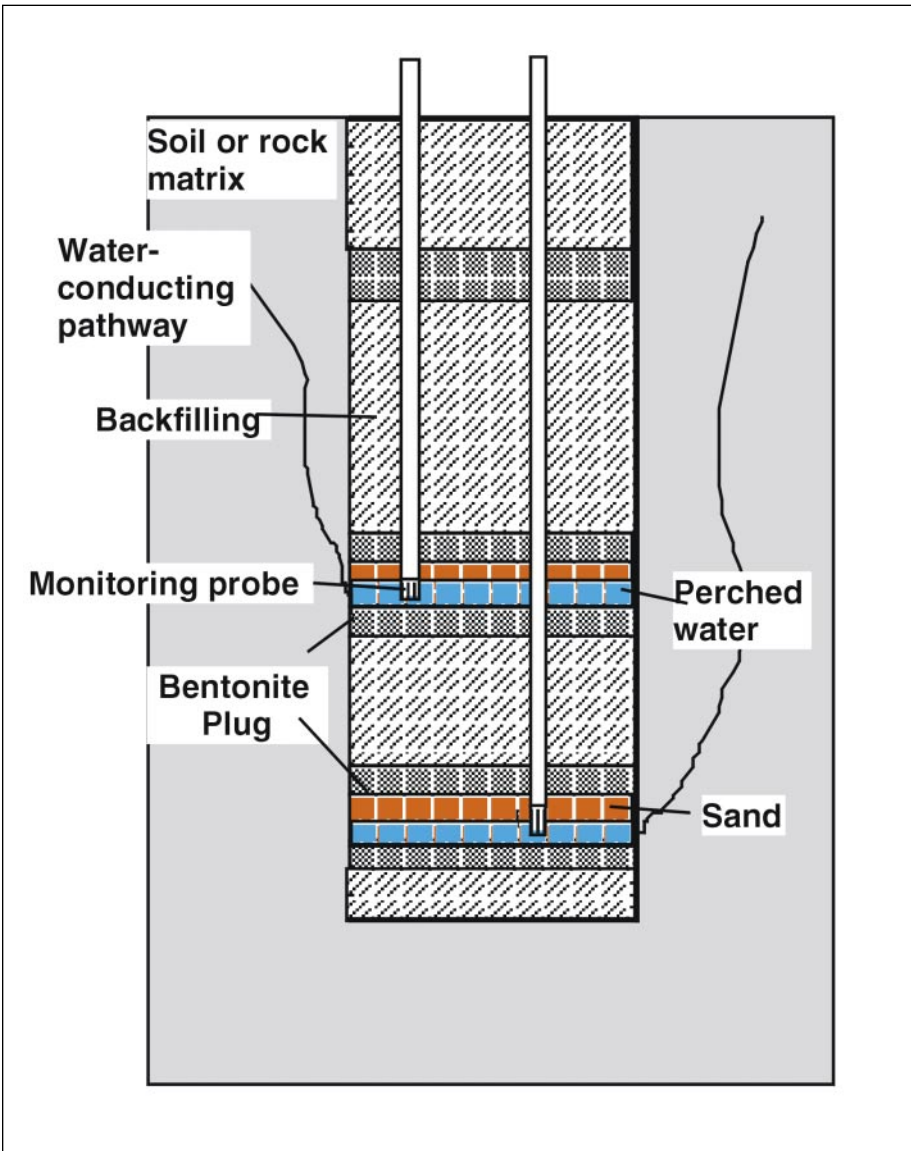


Figure 3-17. Conventional method of installing instrumentation in boreholes (Faybishenko *et al.*, 1998)

The case study ""Gamma Borehole Logging for Vadose Zone Characterization Around the Hanford High-Level Waste Tanks,"" by David S. Shafer, Desert Research Institute; James F. Bertsch and Carl J. Koizumi, MACTEC-ERS; and Edward A. Fredenburg, Lockheed Martin Hanford Company, describes the application of the Spectral Gamma Logging System(SGLS) at Hanford. See page 445.



borehole annulus, which led to the accelerated migration of radioactive and organic contaminants toward the groundwater.

An innovative technology of borehole sealing and instrument installation involves the use of polyurethane grout, which is schematically shown in Figure 3-18. For this method, monitoring probes are installed in contact with natural soils or rocks exposed on the borehole walls using permanently inflatable packers. The procedure is as follows:. Plastic packers are attached to a special 2-in. PVC pipe, and monitoring probes (including tensiometers, suction lysimeters, thermistors, electrical-resistivity sensors, and TDR probes) are taped to the outer surface of the plastic packers. The pipe, assembled with packers and instrumentation, is lowered into a borehole at a field site. Pipes 10 to 20 ft long can be lowered manually, and pipes 40 to 60 ft long are lowered using a boom-truck. After the pipe and string of monitoring probes are placed in a borehole, a water-activated polyurethane resin is injected in the plastic packers. When polyurethane is foamed inside the packer, the packer forces the probes toward the borehole wall. Then, polyurethane is injected in the space between the packers to fully grout the well and to prevent water from entering it.

This technology was tested in fractured basalt with positive results (Faybishenko *et al.* 1999a,b). Based on the testing of the polyurethane resin on Idaho soils and basalts, polyurethane has the following attributes favorable for permanent well completion:

- It adheres well to dry and wetted materials including soils, sediments, and rocks, and will not affect contaminant transport.
- It comes in liquid form, and therefore can easily be injected through a small-diameter tube to infill an annular space of boreholes. The polyurethane set time can be regulated.

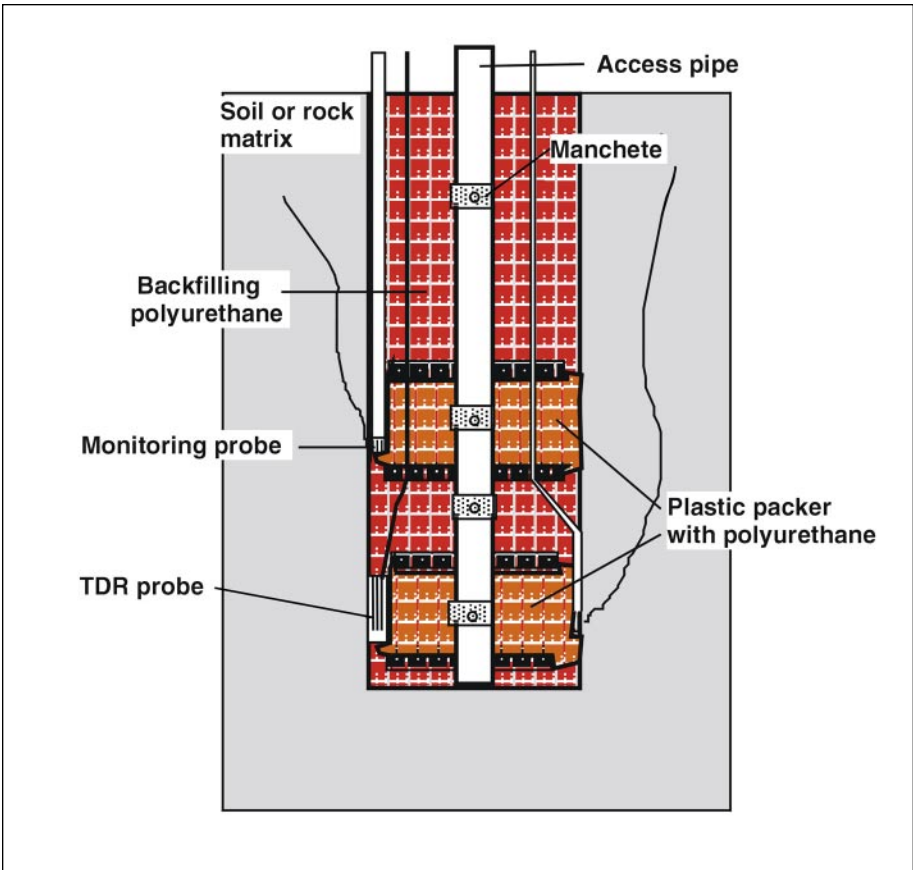


Figure 3-18. Schematic of installing instrumentation and grouting a borehole using polyurethane (Faybishenko *et al.*, 1998)

- It has very low bulk density and electrical properties, which are favorable for geophysical logging.
- Unlike bentonite and cement, it will not change the moisture content of surrounding rocks.
- The use of acrylic casings grouted with polyurethane in boreholes may increase the accuracy of neutron logging (Zawislanski and Faybishenko 1999).

Removable SEAMIST (a. k. a. FLUTe™Systems) Liners*

SEAMIST is an innovative technology that can function both as a borehole casing and as a support platform for sampling devices and instrumentation. SEAMIST consists of the borehole liner of a tubular, impermeable membrane, and a tether that gathers the bottom of the membrane, extends up the center of the hole, and travels to a reel in a canister at the surface (Keller 1991). SEAMIST employs an everting/inverting, flexible liner to seal and support an open borehole while carrying instruments into place and isolating them one from another (Figure 3-19). The everting liner is driven into the hole by air

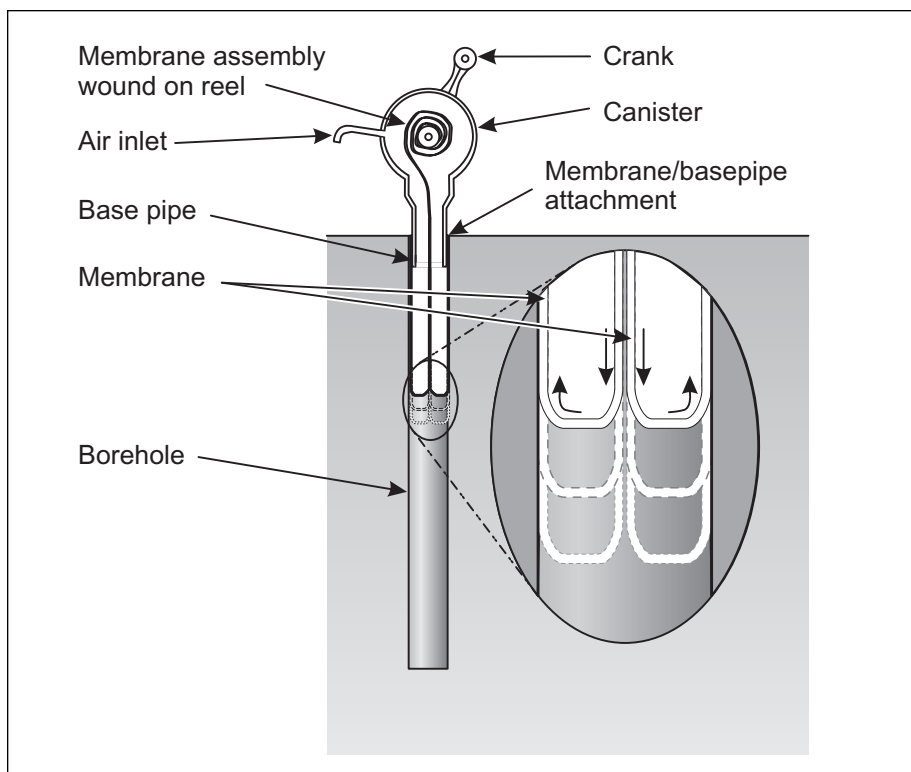


Figure 3-19. Components of a SEAMIST System

*This section was contributed by Carl Keller and Cecelia V. Williams.

pressure. As the liner is propelled into the hole, it carries a variety of “instruments” into place, and seals the holes between the instruments.

Using the apparatus shown in Figure 3-19, the impermeable membrane is emplaced downhole at a speed between approximately 20 to 50 ft/min. Positive pressure is supplied to maintain the integrity of the borehole once the liner is emplaced. Grout or a filler material such as sand may be used instead of air for long-term installations. Because the filler material is located inside the liner, contamination of the geologic medium by the filler is prevented. If the system is later removed from the subsurface, the membrane is wound onto the reel and into the canister by inversion. Therefore, no cross-contamination of absorbent pads or sensors can occur as the membrane is removed. Liners can be made of a wide variety of impermeable materials, including plastic tubular films and laminates. Liner materials are selected on the basis of cost, durability, fabrication ease, impermeability, and chemical compatibility.

SEAMIST liners have been used in horizontal, vertical, enlarged, constricted, and curved holes, and in open and cased boreholes. They can line the borehole temporarily or permanently, preventing the collapse of the borehole, limiting movement of air into the subsurface, and blocking fluid flow into and within the borehole. Sampling ports with attached tubes extend to the surface, while larger instruments (such as gamma logs, neutron logs, resistance logs, and television cameras) can be carried into the hole on the tether. The sample collection instruments that have been emplaced downhole include:

- Absorbers pressed against the hole wall for wicking of liquid samples
- Absorbent material that completely covers the SEAMIST liner from top to bottom of the borehole, allowing a continuous map of the subsurface to be obtained at that location
- Gas-sampling ports and tubing for vapor collection in discrete intervals of the borehole
- Electrical contacts for resistance measurements.

Many of the problems with conventional vadose zone monitoring techniques are eliminated or minimized by the SEAMIST design. These

include: borehole instability, single-point sampling with screened wells, the inability to retrieve and repair instrumentation buried in backfill, and cross-contamination of samples as a result of inadequate backfill seals. These advantages are achieved with a portable, lightweight, and robust emplacement system that is fast and relatively inexpensive. The primary limitation of the technology is that the borehole must remain open long enough after drilling to allow deployment of the membrane (usually less than 30 minutes). If regions of swelling clays are encountered in the lithology, the air-pressurized membrane may not prevent closure of the borehole, unless the liner is sand-filled. The seal of the interface between the membrane and the borehole wall may not be as absolute as in a grouted hole, but appears to be adequate for most applications.

The basic everting liner method has evolved into a large family of techniques for vadose zone measurements. The Duet™ uses two liners: the first liner supports and seals the hole, and the second, instrumented, liner, is deployed in parallel in the same hole, and is used to provide measurements at any place or time without violating the seal or the borehole support. The LAHD™ (Liner Augmentation of Horizontal Drilling) application uses a propagating liner to support a horizontal hole while the hole is being reamed by a horizontal drill rig. The result is an exceptionally clean, sealed hole with little mud invasion, no mud cake, and complete support against hole collapse.

The liner is also used to case and/or instrument the horizontal hole while fully supported. The everting liner can be deployed in cone penetrometer holes and through cone penetrometer rods to emplace the reactive ribbon. The multilevel sampling in the vadose zone has been extended to ground water sampling with a downhole pump for each port. Table 3-7 summarizes SEAMIST applications at various field sites.

Removable Automatic Pneumatic Packers*

Automatic pneumatic injection packers can be used to provide controlled, site-to-site, and borehole-to-borehole testing of stable soils and rocks using the same packer design for injection, pumping, and observations. This approach is amenable to the automation and remote control

*This section was contributed by P. Cook.

TABLE 3-7 Summary of SEAMIST Field Applications

APPLICATION	DESCRIPTION	SITE	PERIOD OF USE
Tritium Plume Monitoring	Two systems are used for tracking the movement and concentrations of a tritiated water plume (both vapor and liquid water sampling to 40 ft).	Lawrence Livermore National Laboratory(LLNL), CA	May 1991 to present
Carbon Tetrachloride Monitoring	Two systems with disposable membrane liners are in use in a carbon tetrachloride plume. The membranes pack off the cased borehole while sample tubing to the bottom draws the vapor sample.	Hanford, WA	1992 to present
Fracture Flow Mapping and Rate Measurement	Membranes coated with liquid-indicating and wicking layers mapped and measured brine flows (grams per day) underground at Waste Isolation Pilot Project, NM.	Waste Isolation Pilot Project, NM	January 1992
Tritium and VOC Sampling	Vapor sampling tubes and absorbent collectors 230 ft were installed horizontally underneath an old radwaste landfill.	Los Alamos National Laboratory (LANL)	April 1992
Sandia National Laboratory - Integrated Demonstrations	<ul style="list-style-type: none"> • Gas sampling and permeability measurements in two boreholes (11.5 in. in diameter and 110 ft deep) • Three 110 ft borehole liners to support holes during logging. 	The Chemical Waste Landfill Sandia National Laboratory (SNL)	Spring through Fall 1992
Vapor Sampling/ Permeability Measurements	Three membranes were instrumented and installed for sampling soil vapor, vapor pressure and permeability measurements. Maximum depth is 130 ft with ten sampling elevations per membrane.	Savannah River Site (SRS)	July 1992 (Continuing for up to 2 years)
Neutron Logging Tool Transport	Neutron moisture logging in horizontal boreholes underneath waste landfill in four boreholes (200 to 250 ft long)	LANL	August 1992
Vapor Sampling	Vapor-sampling with nine sampling points installed to 90 ft deep.	Tucson	September 1992
High Pressure Borehole Liners	Two Kevlar-reinforced membranes were installed to a depth of 155 ft, then filled with water inside cased wells to prevent collapse of the PVC casing during steam injection remediation experiments.	LLNL	October 1992
Borehole Liner	A SEAMIST liner was installed to support/ seal hole while long-term monitoring system is designed.	Utica, NB	October 1992

continued

TABLE 3-7 Summary of SEAMIST Field Applications (*continued*)

APPLICATION	DESCRIPTION	SITE	PERIOD OF USE
Sandia National Laboratory–Integrated Demonstration	Installed gas-sampling tubing to 393 ft in a horizontal borehole of 4 in. in diameter.	SNL	Fall 1993 to Fall 1994
Monitor Fuel Oil Plume Position	Monitor the position of the plume via closely spaced soil vapor sampling ports in a vertical hole.	Swedish Hospital	May 1993 to present
Stabilization of Contamination	SEAMIST is being used to apply strip coat to the interior of ducting to immobilize hazardous dust (such as U and Pu)	Old plutonium facility	Spring 1994
Monitoring of Soil Vapor Extraction	Nine vertical SEAMIST systems with 10 vapor sampling ports to 80 ft used for pressure, permeability, and concentration monitoring.	Sacramento Army Depot, CA	March 1994 to present
Mapping of Contamination at Radioactive Waste Site	Installation, in a mole hole 4.5 in. in diameter, of an absorbent covering on SEAMIST	Oak Ridge WAG6	August 1994 to present
Monitoring of a Radioactive Waste Landfill	Use of SEAMIST in tunnels built in trenches below low-level radioactive waste landfill to monitor for leachate migration.	TA-54, Pit 39	September 1994 to present
Sampling at Discrete Levels below the Water Table	Installation of SEAMIST with water and vapor sampling ports. The water table is at 40 ft below the surface.	March AFB, Riverside, CA	Being installed
Permeability Measurements	Use of SEAMIST in 60 ft deep hole for measurement of permeability and changes during thermal enhanced vapor extraction.	TA-3, Chemical Waste Landfill	July 1994 to present
Tritium Plume Measurement	Installation of absorbers on SEAMIST membrane to 300 ft for wicking of water in vadose zone.	TA-33	August 1994 to present
Vapor Sampling	Multilevel water sampling to 80 ft below SLW.	Saegertow, PA	September 1997
Vapor Pressure	Pore pressure monitoring to 800 ft.	Nevada Test Site, NV	1995 to present
Monitoring	Landfill monitoring in horizontal holes.	Los Alamos, NM	April 1998 to present

continued

TABLE 3-7 Summary of SEAMIST Field Applications (*continued*)

APPLICATION	DESCRIPTION	SITE	PERIOD OF USE
Vapor Sampling	Installation in Sonic Casing to 300 ft.	Asuza, CA	October 1997 to present
Liquid Sampling	Groundwater Sampling (6 ports in 3 in. hole)	Milford, NH	November 1998 to present
Vapor Sampling and Absorber Installations	Duet™ double liners	Yucca Mt., NV	September 1997 to present
Vapor Sampling	Gas sampling in CPT holes	Savannah River Site, SC	September 1997
DNAPL Location	Installation of color-reactive ribbon	Savannah River Site, SC	August 1998
Liquid Monitoring	Absorbers for fracture flow	Yucca Mt., NV	1998

Trademarks: SEAMIST, Robert Alpert Companies
 FLUTe, Duet, LAHD, Flexible Liner Underground Tech.

necessary to establish consistent testing regimens and to accommodate the large number of tests. The packers developed at LBNL for air injection tests (Cook 1999) include inflatable rubber sealing bladders on a packer string, which can be manipulated independently and can divide a borehole into a number of separate zones over the length of the string (Figure 3-20). Each zone is serviced by one 3.2-mm-diameter port for pressure measurement and one 6.4-mm-diameter port for air injection. Several boreholes may be instrumented at one time. A modular design allows partial dismantling of the packer strings in the field for repair or work in tight quarters.

If all the bladders were to be inflated at once, the packer string would seal the entire borehole section that it occupied. However, by inflating every other bladder and allowing the remainder to remain deflated, an alternating sequence of open and closed (sealed) intervals is produced. Depending on the injection control valves, an open interval becomes a pressure monitoring zone, or the injection zone where air is injected during a test. Once tests have been performed with these open zones, the

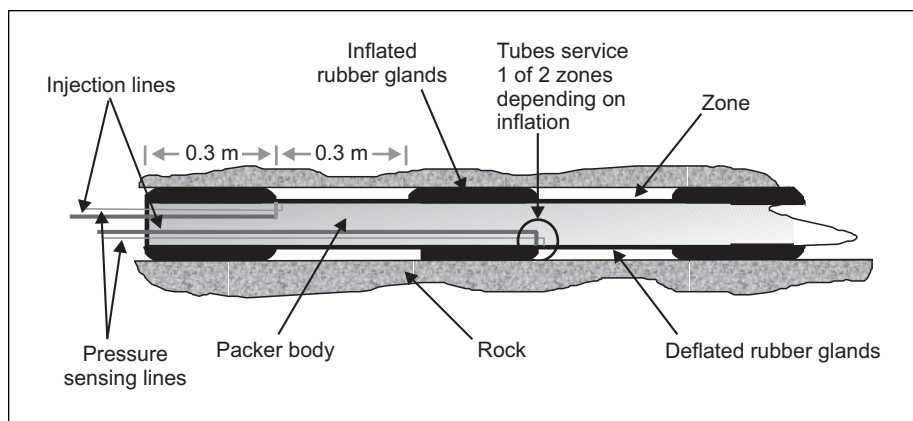


Figure 3-20. Sketch of automatic packer design

inflated bladders are deflated and deflated bladders are inflated, opening those zones that were once sealed, and sealing those that were originally open. In this manner, nearly the entire length of the packer string is usable for testing every 0.3 m without having to move the string. If the zones on the injection packer are changed independently from those on the observation packers, there will be four possible zone configurations available during a given packer installation. Permutations of these injection and observation positions are used to ensure that all positions within each observation borehole are allowed a chance to respond to a given injection zone. The observation packer zones are usually changed in unison, because the locations of the observation zones are thought not to perturb the flow field significantly, and permutations between them would cause only second-order effects in the response system.

Installation of Embedded Sidewall Sensors in Boreholes*

Sensors that are installed in vertical and slanted boreholes at different depths are used to determine matric potential and moisture content, as well as to collect water samples for chemical composition. Sensors placed in boreholes need to be in contact with the formation, as the

*This section was contributed by L. Murdoch and FRx Inc. of Cincinnati.

results of measurements depend on the contact area of the sensors. To address such limitations, Murdoch *et al.* (1999) developed a method for accessing the sidewall of a borehole. The method uses a device that embeds sensors or sediment samplers into the sidewall to distances of about 15 cm (Figure 3-21). The device can also be used to obtain a core sample 15 cm long and 4 cm in diameter, and then to insert a permeable sleeve for extracting samples of water or gas. This device can be used to install several types of electrode sensors, including devices for measuring water content (TDR waveguides), redox potential (platinum-tipped electrodes), or electrical resistivity (a four-conductor, Wenner-type electrode). Horizontally oriented TDR waveguides can be inserted at virtually any depth, thereby extending the TDR technique to the study of deep vadose zones. The borehole is completely sealed to minimize the possibility of cross-contamination after the sensors have been emplaced. The sidewall technique currently can place as many as 60 sensors in a single boring, and offers the potential for markedly increasing the spatial resolution with which processes in the vadose zone can be monitored. The method can be used for embedding sensors in the sidewalls of horizontal or directional boreholes. This application could provide a platform for placing sensors beneath sensitive structures, such as the tanks containing high-level waste at Hanford.

The case study, on the accompanying CD, “Embedded Sidewall Sensors,” L. Murdoch, Clemson University, provides the results of field validation of moisture-content measurements using TDR probes installed at different depths in a vertical borehole sidewall with those from conventional soil sampling. The case study also provides the results of measurements of the redox potential using Eh electrodes installed in the borehole, which would be impossible to do otherwise in the field.

HYDROGEOLOGICAL CHARACTERIZATION USING GEOPHYSICAL METHODS*

Goals of Geophysical Methods and Acquisition Geometry

Geophysical investigations complement hydrogeological methods of site characterization by providing a denser spatial resolution for sub-

*This section was contributed by S. Hubbard, Y. Rubin, and E.L. Majer (LBNL), based on Chapter 10 of *The Handbook of Groundwater Engineering*, by Y. Rubin, S. Hubbard, A. Wilson, and M. Cushey.

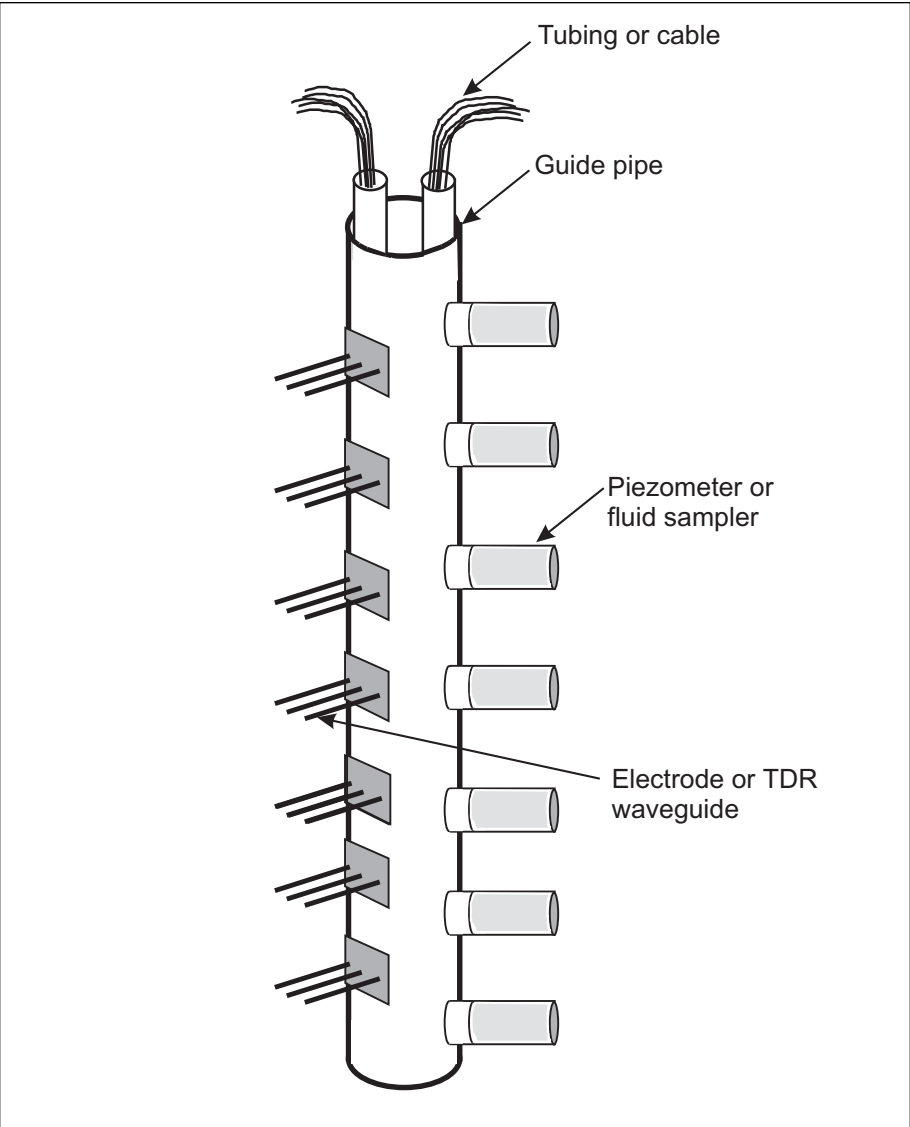


Figure 3-21. Schematic of fluid samplers and electrode sensors embedded in the sidewall of a borehole (after Murdoch *et al.*, 1999)

surface measurements. The main advantage of geophysical investigations is collection of data in a non-invasive manner, which reduces the number of direct measurements needed to fully characterize a site. Figure 3-22 illustrates the resolution and support scale of different types

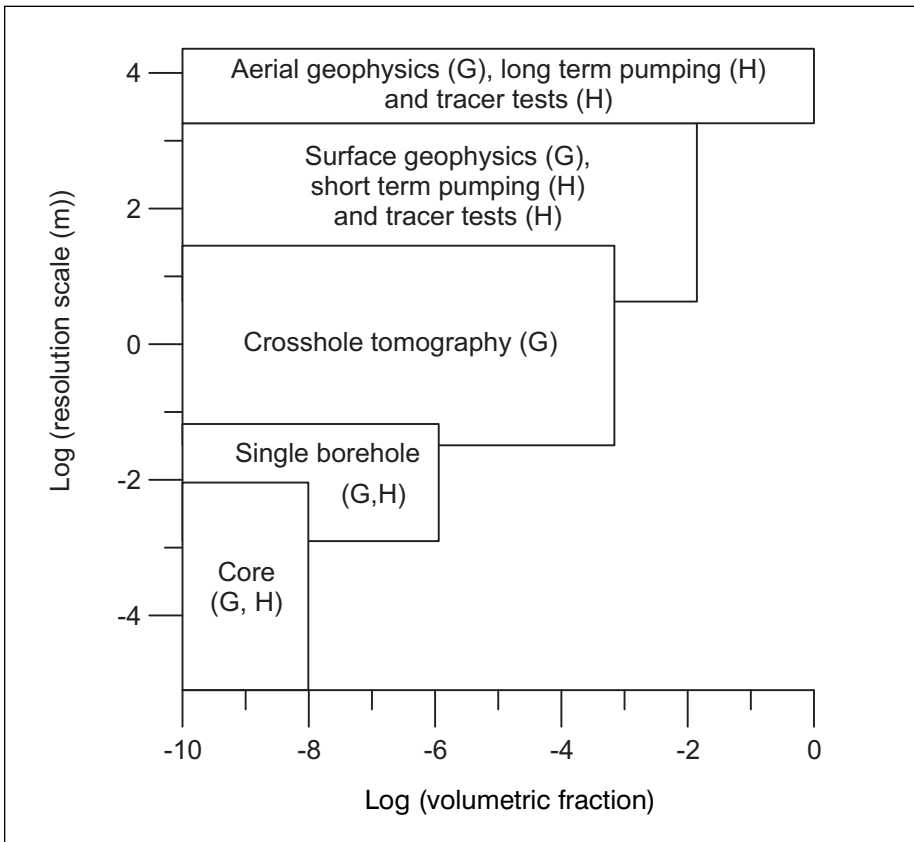


Figure 3-22. Resolution and volumetric fraction of subsurface sampled using hydrological (H) and geophysical (G) characterization methods

of geophysical and hydrogeological measurement techniques. This figure shows that some geophysical techniques have, on average, higher resolutions than others, and that for each method there is a range of possible resolutions. Figure 3-22 also shows that, in terms of both resolution and volume of soil sampled, geophysical data bridge the information gap between the more traditional site characterization techniques of core analysis and borehole testing.

The purpose of this section is to present the main features of geophysical methods that are currently used for near-surface site characterization. The dimensionality and volume of sampled subsurface soil are

in part governed by the acquisition geometry of the geophysical methods. Common acquisition geometries include surface, cross-hole tomographic, and single borehole modes.

Surface geophysical methods are used to detect variations in subsurface properties in one, two, or three spatial dimensions. In electrical-method terminology, the term ‘profiling’ refers to measuring lateral changes in electrical properties over a constant subsurface depth, and the term ‘sounding’ refers to a collection of measurements that are associated with a single surface location and are made as a function of depth. Surface-seismic and ground-penetrating-radar data are displayed as ‘wiggle-trace’ profiles with distance on the horizontal axis and arrival time (which can be converted to depth) on the vertical axis. The vertical and lateral variations in arrival time, amplitude, and phase of the wiggles that comprise the vertical cross-sections are indicative of subsurface physical property changes. Figure 3-23a illustrates how surface radar data are collected by moving the transmitting and receiving antenna across the ground surface and recording the reflected arrivals. Seismic and ground-penetrating-radar profiles yield two-dimensional information about physical property changes.

Cross-borehole tomographic acquisition geometries are used with electrical, seismic, and radar geophysical methods for detailed site investigation. Tomographic data can produce high-resolution images. A typical tomographic geometry consists of two vertical boreholes separated by an interwell region of interest. With this acquisition geometry, sources and detectors are located in separate boreholes. This geometry is illustrated for seismic methods in Figure 3-23b, where direct energy from a source or transmitter in one borehole travels to and is recorded by geophones that are connected by a cable and located in the other borehole. The source position is changed and the recording repeated until the source has occupied all positions in the source borehole. Travel times and amplitudes of the recorded wave are picked and inversion algorithms are used with these data to estimate velocity and attenuation at each cell in the interwell area (Peterson *et al.* 1985). With electrical methods, electrodes occupy the wellbores; with electromagnetic (EM) data, borehole induction coils occupy the wellbores; and with radar methods, antennas occupy the boreholes when collecting tomographic data.

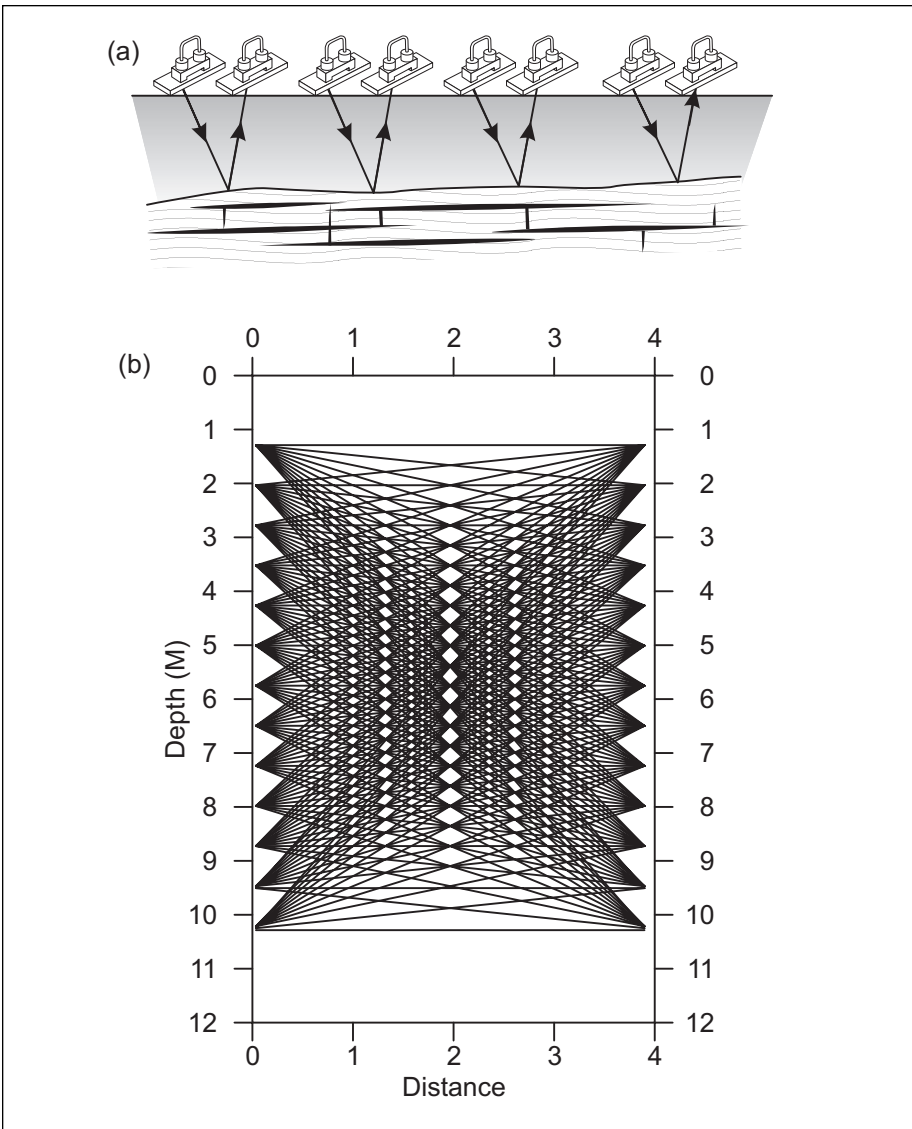


Figure 3-23. Examples of acquisition geometries: (a) Common-offset surface ground penetrating radar acquisition geometry to collect one trace per surface location from a transmitter-receiver pair, and (b) Cross hole tomographic acquisition geometry used for seismic and radar methods. Sources or transmitters and receivers are located in separate boreholes, and energy from each source is recorded at all receivers

Lastly, single downhole acquisition geometries are used with logging tools to sample the physical properties in the vicinity of the wellbore.

Geophysical methods can be used with all of these different acquisition geometries, including surface, tomographic, and single borehole, to collect data at a single point in time as well as over a period of time. Data using “time difference” displays (a data set collected at an earlier time subtracted from a data set collected at a later time) enhances the image of subtle geophysical attribute changes, for example, caused by steam flooding, hydraulic fracturing, or the spread of contaminant plumes.

The particular geophysical method and acquisition geometry used for a given investigation is chosen by considering the investigation target, the necessary level of resolution, conditions of the site, funds available for the investigation, and the availability of other data. In the following sections, we present the concepts of several geophysical methods, including electrical, seismic, gravity, and magnetic techniques. All of these methods can be employed using surface-acquisition geometries, and it is also becoming more commonplace to collect electrical and seismic data using tomographic geometries. Tables 3-8 and 3-9 summarize potential applications and limitations of the different surface or tomographic techniques, as well as the frequency of use, relative cost, and relative resolution of each method. Table 3-8 also lists the geophysical attribute that is commonly measured using each technique. For hydrogeological characterization, it is common to transfer these geophysical attributes into hydrogeological parameter estimates using petrophysical relationships (Rubin *et al.* 1998). For more detailed information about these individual geophysical methods, refer to Telford *et al.* (1990) and Robinson and Coruh (1988). Single wellbore logging methods are discussed separately below, and Tables 3-10 and 3-11 provide a summary of potential applications and limitations of these borehole techniques.

Electrical Methods

Electrical methods involve the detection of the effects of electric current flow in the soils. The two properties of primary interest are (1) the ability of a material to conduct electrical current, or the electrical conductivity, and (2) the displacement current, which occurs when an electrical current is passed through the material (that is, the dielectric

TABLE 3-8 Surface and Crosshole Geophysical Methods, Parameters, Potential Applications, and Limitations

Method	Parameters Commonly Inferred from Measurements	Potential Applications	Limitations	Relative Cost* ¹	Relative Resolution* ²	Frequency of Use for Site Characterization
ELECTRICAL						
DC Resistivity	Electrical Resistivity	<ul style="list-style-type: none"> • Mapping of: gross stratigraphy, faults, depth to bedrock fresh/salt water interfaces, landfills, and some contaminant plumes 	<ul style="list-style-type: none"> • Can not be used in paved areas • Wires can be cumbersome, and arrays can be long for deep investigations 	Moderate-high	Moderate	Very common
EM	Electrical Conductivity	<ul style="list-style-type: none"> • Mapping of: gross stratigraphy, salt/fresh water interfaces, depth to bedrock, faults, and some contaminant plumes • Detection of buried tanks and pipes 	<ul style="list-style-type: none"> • Difficult to resolve resistive targets, noise from power lines, and fences and pipes 	Low-moderate	Moderate	Very common
GPR	Dielectric Constant	<ul style="list-style-type: none"> • Mapping of: detailed stratigraphy, some contaminant plumes, cavities, depth to bedrock, and water table • Detection of buried tanks and pipes • Estimation of hydrogeologic properties using petrophysical relationships and tomographic or CMP acquisition geometries 	<ul style="list-style-type: none"> • Ineffective in highly electrically conductive environments, due to interference from electrical noise such as power lines and fences • Hydrogeologic property estimation entails more sophisticated data acquisition and processing procedures 	Moderate	High	Very common (surface GPR) Uncommon (tomographic or CMP GPR)
SEISMIC						
Reflection	P-wave reflectivity and velocity	<ul style="list-style-type: none"> • Mapping of: gross and detailed stratigraphy, faults, and water table 	<ul style="list-style-type: none"> • Acquisition often difficult in unconsolidated environments • Sophisticated acquisition and processing system required • Sensitive to cultural noise 	Moderate-high	High	Common

continued

TABLE 3-8**Surface and Crosshole Geophysical Methods, Parameters, Potential Applications, and Limitations** *(continued)*

Method	Parameters Commonly Inferred from Measurements	Potential Applications	Limitations	Relative Cost* ¹	Relative Resolution* ²	Frequency of Use for Site Characterization
Crosshole	P-wave velocity and attenuation	<ul style="list-style-type: none"> • Mapping of: detailed stratigraphy, faults, cavities, and some contaminant plumes • Estimation of porosity and permeability using petrophysical relations 	<ul style="list-style-type: none"> • Sophisticated acquisition and processing necessary • Sensitive to cultural noise • Best in saturated sections 	High	High	Uncommon
Refraction	P-wave velocity	<ul style="list-style-type: none"> • Mapping of: gross stratigraphy and velocity structure, depth to bedrock, water table, and significant faults 	<ul style="list-style-type: none"> • Gross feature identification only • Can not resolve low layers that have lower velocities than overlying layers • Sensitive to cultural noises 	Low	Low	Common
GRAVITY AND MAGNETICS						
Gravity	Density	<ul style="list-style-type: none"> • Mapping of: depth to bedrock, faults, landfills, and cavities 	<ul style="list-style-type: none"> • Gross feature identification only • Requires extensive data reduction and accurate elevation information 	Low-moderate	Low	Uncommon
Magnetics	Presence of magnetic materials	<ul style="list-style-type: none"> • Mapping of: depth to magnetic basement, locating buried drums and pipes, and landfill delineation 	<ul style="list-style-type: none"> • Interference from industrial and near surface magnetic features 	Low	Low-high depending on application	Very Common

*¹ Using acquisition parameters that sample similar subsurface volumes.*² Resolution is a function of geophysical method, acquisition parameters, and site conditions. This column presents relative resolutions for acquisition in environments favorable for each method using parameters optimal for a near-surface investigation for that method.

TABLE 3-9**Summary of Possible Applications of Surface and Cross-Borehole Geophysical Methods for Site Characterization**

Surface/Crosshole Method: Application	Resistivity	EM Induction	GPR	Seismic Reflection	Crosshole Seismic	Seismic Refraction	Gravity	Magnetics
Depth to Water Table	2	2	4	2	0	4	1	0
Fresh/Salt Water Interface	4	4	2	1	0	2	0	0
Depth to Bedrock	4	4	4	4	0	4	4	2
Gross Hydro-stratigraphy	4	4	4	4	1	4	1	1
Detailed Hydro-stratigraphy	2	3	4	4	4	1	1	0
Significant Fault Detection	4	4	4	4	4	4	4	4
Cavity Detection	2	1	3	2	3	0	2	1
Porosity, Permeability Estimation	3	3	3	3	3	1	1	0
Water Content Estimation	3	3	3	1	0	1	1	0
Contaminant Detection	3	3	3	1	3	0	0	0
Detection of Buried Metallic Objects	2	4	4	2	1	0	1	4
Landfill Delineation	4	4	4	2	2	2	2	4

Key:

0 = not considered applicable

1 = limited use

2 = used, or could be used, but not the best approach or has limitations

3 = excellent potential but not fully developed

4 = generally considered an excellent approach, techniques are well developed

TABLE 3-10

Summary of Physical Property Measured, Applications and Limitations of Borehole Geophysical Methods

Borehole Tool	Measurement	Applications	Limitations and Sources of Error	Frequency of Use for Groundwater Characteristic	Borehole Conditions	Radius of Investigation
Caliper	Borehole diameter	<ul style="list-style-type: none"> Borehole diameter measurement, fracture detection, and lithology inference 		Common	<ul style="list-style-type: none"> Cased or uncased Saturated or unsaturated 	Borehole wall only
Electrical Induction	Electrical Conductivity	<ul style="list-style-type: none"> Lithological identification, clay content, and lithology inference 	<ul style="list-style-type: none"> Works best for delineating electrically conductive targets, affected by resistivity of borehole fluid 	Uncommon	<ul style="list-style-type: none"> Uncased or PBC cased Saturated or unsaturated 	¼ m to several m from borehole wall
Nuclear Gamma	Natural gamma	<ul style="list-style-type: none"> Lithological identification, clay content, and permeability estimation 	<ul style="list-style-type: none"> Affected by casing, cement, mud, borehole diameter, and position of probe in well 	Common	<ul style="list-style-type: none"> Cased (PVC or steel) or uncased Saturated or unsaturated 	15-30 cm from borehole wall
Gamma Spectrometry	Natural gamma radiation	<ul style="list-style-type: none"> Lithological identification Identification of radioisotopes in groundwater 	<ul style="list-style-type: none"> Affected by borehole diameter, fluid, casing, annular material, and instrument drift Requires computer analysis 	Uncommon	<ul style="list-style-type: none"> Cased (PVC or steel) or uncased Saturated or unsaturated 	15-30 cm from borehole wall

continued

TABLE 3-10 Summary of Physical Property Measured, Applications and Limitations of Borehole Geophysical Methods

Borehole Tool	Measurement	Applications	Limitations and Sources of Error	Frequency of Use for Groundwater Characteristic	Borehole Conditions	Radius of Investigation
Gamma-Gamma or Density	Electron density	<ul style="list-style-type: none"> Lithologic and depth to bedrock identification, density, porosity, and moisture content estimation 	<ul style="list-style-type: none"> Affected by borehole diameter, gravel pack, casing, mud cake, cement, and position of probe in hole 	Common	<ul style="list-style-type: none"> Saturated or unsaturated Optimal in uncased 	15 cm from borehole wall
Neutron	Hydrogen content	<ul style="list-style-type: none"> Moisture content, saturated porosity, lithology, and depth to water table 	<ul style="list-style-type: none"> Affected by borehole diameter, thickness of mud cake, casing, cement, mud weight, temperature, and pressure Source requires license 	Common	<ul style="list-style-type: none"> Saturated or unsaturated Optimal in uncased 	15-25 cm from borehole wall
Acoustic Acoustic, Sonic or Velocity	P-wave transit time	<ul style="list-style-type: none"> Lithology and fracture identification Depth to bedrock, estimation of grout integrity and porosity 	<ul style="list-style-type: none"> Spikes occur when amplitude of P-wave is less than detection level of tool Dry hole sondes can be used in vadose zone 	Common	<ul style="list-style-type: none"> Conventional—Uncased and Dry hole sondes—Uncased and unsaturated 	25 cm for sediments, 120 cm for rocks

TABLE 3-11

Summary of Possible Applications of the Most Common Borehole Geophysical Methods for Site Characterization

Borehole Method: Application:	Caliper	Induction	Gamma	Gamma- Gamma (Density)	Neutron	Borehole Imager
Lithology	4	4	4	4	4	4
Fracture Detection	4	2	0	0	0	4
Porosity Estimation	0	3	1	4	4	3
Moisture Content	0	2	0	4	4	3
Permeability Estimation	0	3	3	2	2	2
Water Quality	0	3	2	0	2	2

Key:
0=not considered applicable
1 = limited use
2 = used, or could be used but not the best approach or has limitations
3 = excellent potential, but not fully developed
4 = generally considered an excellent approach, techniques are well developed

properties). In the following paragraphs, we review the most commonly used electrical methods for near-surface investigations of electrical resistivity, electromagnetic techniques, and ground-penetrating radar.

Resistivity

Resistivity is a measure of the ability of current to flow through a given material, and is an intrinsic property of the material. Resistivity methods involve the introduction of a direct current (DC) or very low frequency (less than 1 Hz) current into the ground between two current electrodes. In a two-electrode system, current flows from the positive current electrode to the negative current electrode. These currents establish equipotential surfaces, and current flow lines are perpendicular to these surfaces. To deduce the subsurface resistivity, we place two potential electrodes between the current electrodes to measure the difference in potential or voltage. These measurements, together with the known current and a geometric factor (which depends on the particular elec-

trode configuration), can be used to calculate resistivity following Ohm's law.

No other physical property of naturally occurring material displays such a large range of values as electrical resistivity, which commonly varies over 12 orders and has a maximum range of 24 orders of magnitude (Zohdy *et al.* 1974; Telford 1990). This wide range has rendered electrical resistivity a useful tool for mapping subsurface structure and stratigraphy, and for estimating hydrogeological parameters. In general, the electrical resistivity is reduced with an increase in water content and salinity, an increase in clay content, and a decrease in grain size (Burger 1992). Because of the myriad of factors affecting electrical resistivity measurements, it is often difficult to directly correlate resistivity with lithology without other constraining information. However, general statements can be made regarding electrical resistivity values, such as: (1) resistivity is sensitive to moisture content, and thus, unsaturated sediments usually have higher resistivity values than saturated sediments, (2) sandy materials generally have higher resistivity values than clayey materials, and (3) granitic bedrock generally has higher resistivity values than saturated sediments and often offers a large apparent resistivity contrast when overlaid by these sediments. Reviews of the resistivity method are given by Ward (1990), Van Nostrand and Cook (1966) and Zohdy *et al.* (1974).

Electromagnetic Induction

The use of electromagnetic techniques for environmental site assessments has increased dramatically in recent years. Controlled-source inductive EM methods use a transmitter to pass a time-varying current through a coil or dipole on the earth's surface. This alternating current produces a time-varying magnetic field, which interacts with the conductive subsurface to induce time-varying eddy currents. These eddy currents give rise to a secondary EM field. Attributes of this secondary magnetic field, such as amplitude, orientation, and phase shift, can be measured by the receiver coil. By comparing these attributes with that of the primary field, information about the presence of subsurface conductors, or the subsurface electrical conductivity distribution, can be inferred. Electrical conductivity is the inverse of electrical resistivity, which is measured using resistivity techniques. As such, electrical conductivity measurements are also affected by material texture, porosity,

presence of clay minerals, moisture content, and the electrical resistivity of the pore fluid. EM methods tend to require less time, and achieve greater penetration depth with shorter arrays than DC resistivity methods. However, the EM equipment can be more expensive, and the interpretational methods necessary to extract qualitative information can be more complicated than those used with resistivity methods. In general, EM methods are best suited for use when attempting to detect the presence of high-conductivity subsurface targets such as salt-water saturated sediments. Reviews of the instrumentation available for EM induction systems, their applicability for environmental site characterization, and EM interpretational methods are given by Hoekstra and Blohm (1990), Goldstein (1994) and McNeill (1990).

Ground-Penetrating Radar

Ground-penetrating radar (GPR) is a relatively new geophysical tool that has become increasingly popular with the growing need to better understand hydrogeological conditions. GPR methods use electromagnetic energy at frequencies of 10 to 1000 MHz to probe the subsurface. At these frequencies, dielectric properties (that is, the separation, or polarization, of opposite electric charges within a material that has been subjected to an external electric field) dominate the electrical response. GPR systems include an impulse generator, which repeatedly sends a particular voltage and frequency source to a transmitting antenna. A signal propagates from the transmitting antenna through the earth and is reflected, scattered, and attenuated by variation in subsurface dielectric contrasts. Subsequently, the modified signal is recorded by the receiving antenna. In general, GPR performs better in unsaturated coarse or moderately coarse textured soils. GPR performance is often poor in electrically conductive environments such as saturated, clay-rich, or saline soils.

Estimation of the dielectric constant is necessary to infer quantitative hydrogeological information from GPR data. For the high frequency range of interest for GPR methods, the propagation phase velocity (V) in a material with low electrical conductivity can be related to the dielectric constant (κ) as:

$$\kappa \approx \left(\frac{c}{V} \right)^2 \quad (3.1)$$

where c is the propagation velocity of electromagnetic waves in free space, or the speed of light, of 3×10^8 m/sec (Davis and Annan 1989). Equation 3.1 enables the estimation of dielectric information from radar signal propagation velocity estimates, which can be extracted from radar data collected with common midpoint (CMP) or tomographic acquisition geometries. Dielectric constants are affected by material saturation, porosity, material constituency, temperature, and pore fluid composition. The dielectric constant of air and water are 1 and 80, respectively; most dry materials have dielectric constants of 3 to 7; most wet materials have dielectric constants of 15 to 30. Surface radar profiles are commonly used for mapping stratigraphy and structure. Dielectric constant values obtained from radar data in surface CMP or tomographic modes can be used to estimate characteristics such as soil saturation.

Seismic Methods

Seismic reflection, cross-hole transmission, and refraction methods use artificially generated, high-frequency (100 to 5000 Hz) pulses of acoustic energy to probe the subsurface. These disturbances are produced at a point and propagate outward as a series of wavefronts. The passage of the wavefront creates a motion that can be detected by a sensitive geophone and recorded on the surface. According to the theory of elasticity upon which seismic wave propagation is based, compressional, shear, and surface waves are produced by a disturbance, and each wave travels with a different propagation velocity. Because of the relative ease of detecting the compressional (or P-wave) energy, the most common surface seismic acquisition modes of reflection and refraction have been designed to provide information about this wave.

Seismic data are also collected using cross-borehole tomographic acquisition modes. Because of the high resolution offered by seismic tomographic methods, this technique is ideal for detailed stratigraphic and hydraulic characterization of interwell areas.

Reflection

The surface reflection technique records the return of reflected compressional waves from boundaries where acoustic contrasts exist. Seismic reflection data are usually collected as common-shot or common-receiver gathers, which are sorted during processing into

common-midpoint gathers. These gathers of traces represent reflections from a subsurface location (the midpoint) that has been sampled by several source-receiver pairs. Due to the lack of well-defined velocity contrasts in unconsolidated and unsaturated materials, seismic reflection data acquisition is often difficult in the vadose zone. Computer-based processing of seismic reflection data generally produces a wiggle-trace profile that resembles a geologic cross section. In addition to obtaining structural and stratigraphic information about the subsurface from the wiggle traces, information about seismic velocity is available through seismic data processing (Yilmaz 1987).

Seismic compressional wave velocity is affected by porosity, permeability, pore fluid type, depth of burial, consolidation, and temperature. However, unique relations between seismic P-wave velocities and lithology generally do not exist. Some generalities can be made regarding the relationship between seismic velocities and lithology (Burger 1992), including:

- Unsaturated sediments have lower velocities than saturated sediments
- Unconsolidated sediments have lower velocities than consolidated materials
- Velocities are very similar in saturated, unconsolidated sediments
- Weathered rocks have lower seismic velocities than unweathered rocks of the same type

Refraction

With refraction methods, the incident ray is refracted along the target boundary before returning to the surface. The refracted energy arrival times are displayed as a function of distance from the source. The arrival times and distances can be used to directly obtain velocity information. Refraction techniques are useful when there are only a few shallow (less than 50 m in depth) targets of interest, or for identifying gross lateral velocity variations or changes in interface dip (Lankston 1990). Seismic refraction methods yield a much lower resolution than seismic reflection and crosshole methods. Because refraction methods are cheap and acquisition is sometimes more successful in unsaturated and unconsolidated environments, these methods are often used to detect the depth to

the water table and top of bedrock, the gross velocity structure, and the location of significant faults. A review of the refraction method is given by Lankston (1990).

Gravitational Methods

Measurements of the changes in gravitational acceleration can be used to obtain information about subsurface density variations. As density is a bulk property of rocks and tends to be consistent throughout a geological formation, gravity methods are used to identify gross features based on density variations. Because of the lower resolution afforded by this method, it is not commonly used for detailed site characterization. It does, however, provide a cheap way to detect some targets, such as the interface between sedimentary overburden and bedrock, or the locations of significant faults. Gravity methods have also been used to detect sinkholes and other subsurface voids, and to establish landfill boundaries. The common measuring device is a gravimeter, which is a portable and easy-to-use instrument. A spring balance inside the gravimeter measures differences in the weight of a small internal object from location to location, which are attributed to changes in the acceleration of gravity resulting from lateral variations in subsurface density. Measurements can be collected at a regional or local scale depending on the station spacing. The station spacing is usually less than half of the depth of interest. Reviews of the gravity technique and applications to environmental studies are given by Hinze (1990) and Butler (1991).

Magnetic Methods

Magnetic methods are used to detect the direction, gradient, and intensity of the earth's magnetic field. The intensity of the magnetic field at the earth's surface is a function of the location of the observation point in the primary earth magnetic field, as well as local or regional concentrations of magnetic material. Magnetometers are used to measure the total geomagnetic field intensity or relative values of the vertical field intensity; magnetic gradiometers measure the horizontal and vertical gradient of this magnetic field. After correcting for the effects of the earth's natural magnetic field, magnetic data can be presented as total-intensity, relative-intensity, and vertical-gradient-anomaly profiles or contour maps. Magnetic solutions are non-unique, and interpretation

generally involves forward modeling or mapping of the anomalies and correlating the results with additional geologic information. Magnetic methods are generally used to identify gross features at a resolution similar to that of seismic refraction and gravitational methods. In near-surface studies, magnetic data are commonly used to map the depth to the basement, providing provided that the basement rock contains sufficient magnetic minerals. Sedimentary materials, which are most common in aquifers, are essentially non-magnetic. Magnetic methods with much finer station spacing and higher lateral resolution (a few meters) are now among the most commonly used geophysical methods for site investigation, because of their ability to locate shallow metal objects, such as drums and abandoned drill-hole casings. A review of magnetic methods as applied to environmental problems is given by Hinze (1990).

Borehole Geophysical Methods

Borehole geophysics refers to the process of recording and analyzing physical property measurements made in holes or wells. One-dimensional borehole data can be correlated to extrapolate the information between the wellbores, and can also be used to calibrate surface geophysical data. The volume of investigation for downhole logs is related to log type, source-detector spacing, and subsurface material, and thus varies with the well-site conditions and the logging parameters employed. Interpretation of the recorded log data often involves comparing several different logs displayed side-by-side, or by cross-plotting data from one log against data from other logs, core analysis, or tests. For hydrocarbon exploration, the decision to test and complete a well is largely based on geophysical log information, and, as a result, most of the interpretation guidelines for borehole geophysics have been developed for borehole and rock environments encountered in petroleum exploration. An excellent reference for borehole geophysics applied to groundwater investigations is given by Keys (1989), which is the reference for the following logging information unless otherwise cited. Another one-dimensional sampling tool that is useful for vadose zone characterization is the cone penetrometer (CPT). A complete overview of the CPT method and applications is given by Lunne *et al.* (1997). Both borehole logging devices and CPT tools will be discussed, briefly, below.

Borehole Logging Tools

Borehole log measurements are made by lowering a sonde into the borehole on the end of an electric cable. The sonde is a probe, 2.5 to 10 cm in diameter and 0.6 to 9 m in length, which encloses sources, sensors, and the electronics necessary for transmitting and recording signals. Measurements made in the borehole are recorded on the surface in digital form, or in analog form on chart paper. The following discussion focuses on the underlying physical principles of only those logging methods that are either currently used in vadose zone applications or that have potential for aiding these investigations, including caliper, electric, nuclear, acoustic logging and borehole imaging tools. Table 3-10 lists the applications, limitations, and borehole conditions required for each method, as well as the frequency of use of the method for vadose zone applications. Although some borehole techniques have potential for aiding vadose zone studies, they are nevertheless not commonly used, due to the sophistication, and, thus, higher cost of using the method. Table 3-11 summarizes the applications of some of these borehole geophysical methods. The table refers to information available from individual logs only. More information about fault displacement can be obtained by correlating several logs or by integrating the well logs with surface geophysical methods or other data.

Caliper Logging

Caliper logs are mechanical or acoustic tools that measure the diameter of the borehole. The mechanical caliper tool includes between one and six caliper probes connected to a single arm. The probes are pressed against the borehole wall by spring pressure. As the tool is pulled up the borehole, the mechanical caliper probes move in response to changes in borehole diameter, and the acoustic calipers measure the reflection transit time of an acoustic signal from the borehole wall. Changes in the diameter of the borehole affect the response of all geophysical tools, and therefore, a caliper log is generally collected in conjunction with all logging suites to aid in interpretation and correction of the other logs. Changes in wellbore diameter can be related to casing design as well as to fracturing or caving along the borehole wall, which can sometimes be indicative of the lithology.

Electric Logging

Electric logs measure potential differences resulting from the flow of electric current in and adjacent to the well. There are many different types of electric logs including single-point, resistivity, dipmeter, and spontaneous potential. These logs are often used in groundwater applications to investigate subsurface properties such as lithology, water quality, fracture locations, and porosity. However, because these logs must be run in saturated boreholes prior to casing, their application is limited for vadose zone investigations. An electric log that can be run in unsaturated and uncased borehole environments is the induction log. This tool has two coils: one for transmitting and alternating current into the surrounding formation and a second for receiving the returned signal. The transmitted alternating current induces eddy-current flow in surrounding conductive materials. These eddy currents set up secondary magnetic fields that induce a voltage in the receiving coil; the magnitude of the received current is proportional to the electrical conductivity of the surrounding material.

Nuclear Logging

Nuclear logging entails the detection of unstable isotopes near the borehole. The considerable advantage of nuclear logs over electric logs is that they can be run after casing has been installed. As isotopes decay, they emit radiation, usually from the nucleus. Of the radiation emitted, gamma photons and neutrons are often used in borehole applications because of their ability to penetrate dense material such as rock and casing. Borehole geophysical tools that measure radioactivity of nearby formations may be classified as either those that detect natural gamma radiation, those that employ controlled gamma rays to induce radiation, or those that use neutron sources to induce nuclear processes. The radioactivity is measured as electronic pulses, and the quantity and amplitude of the pulses yield information about the surrounding formation. Logging tools that use artificial radioisotopes as sources are regulated by governmental agencies and require a license for use.

The gamma log uses a scintillation detector to measure the amount of naturally occurring gamma radiation of the material penetrated by the borehole within a selected energy range. The three most common naturally occurring radioactive materials that affect the gamma log are

potassium-40, uranium-238, and thorium-232. The utility of this log lies in the fact that these isotopes are generally more abundant in shales and clays, that the isotopes are less common in sands and calcareous materials, and that reliable measurements can be made above the water table. The gamma log reveals the characteristically high gamma-log count rate associated with silts and clays. In addition to the count rate that is measured with the gamma log, the gamma-spectrometry method records the amplitude of the pulses over a wide energy range. Analysis of this energy yields more diagnostic information on lithology, and also permits estimation of the type and quantity of radioisotopes that may be contaminating the groundwater. Gamma-gamma or density logs record gamma radiation that originates from an artificial gamma source in the well and that is backscattered by the borehole and surrounding material. The count rate of the backscattered gamma rays can be related to the electron density of the material, which is in turn proportional to the bulk density of the material. If the fluid and grain densities are known, the bulk density measured with the gamma-gamma log can be used to calculate porosity. Because moisture content affects the bulk density of materials, gamma-gamma logs can also be used to record changes in moisture above the water table.

Neutron tools consist of an artificial low-energy wellbore neutron source and one or two neutron detectors. The neutrons emitted by the source lose energy upon collision with other elements in the vicinity of the borehole. Because hydrogen has a mass similar to the neutron, it is the element that is most effective at slowing the neutrons. The quantity of slowed neutrons is thus interpreted to be proportional to the quantity of hydrogen present, which is in turn interpreted to be proportional to the moisture content or saturated porosity. For most materials, resistivity and neutron logs have a similar log character because of the relationship between saturated porosity and pore fluid resistivity.

Acoustic Logging

Acoustic (sonic or velocity) tools transmit an acoustic pulse through the fluid and material near the borehole, from a source to the detector. These tools emit an acoustic source at frequencies of 10 to 35 kHz, which creates compressional or P-waves. As the waves travel, some of the energy is refracted back to two receivers located on the sonde. The difference in travel time between the receivers is used to calculate inter-

val velocity, which is recorded as a function of depth in the wellbore. Acoustic waveform logging entails the recording and interpretation of the entire waveform rather than just the travel time. Because conventional acoustic logs require saturated borehole conditions for signal transmission, acoustic logs are not commonly used in the vadose zone. In some circumstances, use of a water-filled casing with an end-cap may allow sufficient coupling for conventional acoustic logs to be used in the vadose zone. Alternatively, dry-hole acoustic sondes exist that can be used in uncased and unsaturated boreholes. Dry-hole sondes can not be used while moving the tool in the borehole, and because there is no contacting fluid with this tool, the signal-to-noise ratio is typically smaller than that for conventional acoustic tools (Hearst and Nelson, 1985).

Borehole Imagers

Borehole cameras or scanners provide very high-resolution video or digital images of the borehole wall. An unfolded borehole image can be thought of as a cylinder that has been opened along a side and flattened to provide a 360-degree picture of the borehole wall. Planar horizontal features that intersect the well appear horizontally, and planar dipping features that intersect the well appear as sinusoids with the lowest point of the curve in the direction of dip.

FIELD MEASUREMENTS OF WATER POTENTIAL

One of the challenging problems of vadose zone investigations is the determination of water potential in unsaturated-saturated heterogeneous soils and fractured rocks. The water potential is a characteristic of the energy status of water in the subsurface. Because the soil matric potential in unsaturated soils and sediments varies in significant range from 0 to -15 bar, there is no single technique to measure over the entire range of the matric potential. The detailed description of field and laboratory methods of measuring the water potential is given in a monograph by Klute (1986). Gee and Ward (1999) presented a thorough review of innovations in two-phase measurements of soil hydraulic properties. Figure 3-24 shows schematically the water pressure ranges for laboratory and field measurements using tensiometers, heat dissipation probes, and thermocouple psychrometers.

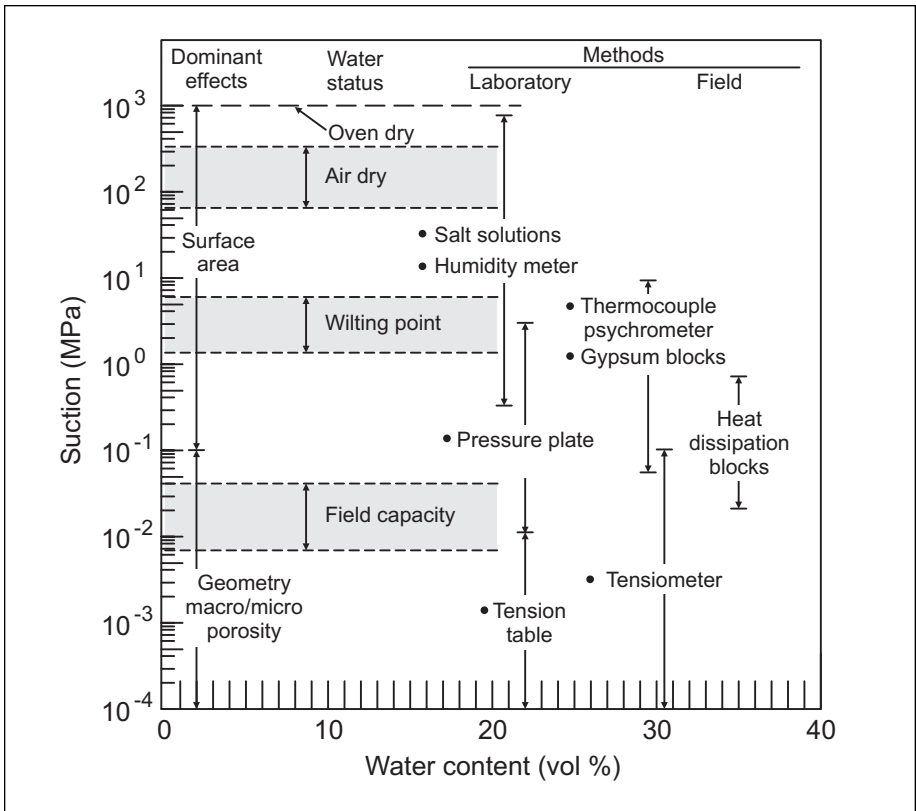


Figure 3-24. Schematic showing the operational ranges of field and laboratory methods used in monitoring the matric suction in the vadose zone for soil water physical processes (Gee and Ward 1999)

General Design and Applications

Tensiometers have been used from as early as the 1920s for a variety of specific applications (Kornev 1924; Richards and Gardner 1936), including water-pressure measurements at hazardous-waste sites (Healy *et al.* 1983; McMahon *et al.* 1985; Ripp and Villaume 1985; Ryan *et al.* 1991); recharge areas (Lichtler *et al.* 1980; Sophocleous and Perry 1985); irrigation land (Richards *et al.* 1973); and for civil-engineering projects (McKim *et al.* 1980; Richards *et al.* 1938). Tensiometers have been used under both laboratory and field conditions in variably saturated porous media to assess the soil-water potential, which is then used to determine

the hydraulic gradient, direction of water flow, and the water flux in soils, as well as to indirectly estimate the soil-water content using water-retention curves (Richards *et al.* 1938; McKim *et al.* 1980; Sposito 1981; Stannard 1986; ASTM 1998; Kutilek and Nielsen 1994).

Although tensiometer design has undergone various changes, its basic components have remained unchanged. A tensiometer is comprised of a porous tip (usually a ceramic or metal cup) connected to a water-filled tube and a pressure sensor. It is advisable to use deaerated water to fill in tensiometer tubes. Pressure sensors commonly used in tensiometers include vacuum gauges, mercury manometers, and pressure transducers (Marthaler *et al.* 1983). Pressure transducers can be connected to tensiometers either remotely (Klute and Peters 1962; Healy *et al.* 1986) or directly (Bianchi 1962; Watson 1967; Hubbell and Sisson 1998).

An expanded cross-sectional view of the interface between a tensiometer porous tip and soil is shown in Figure 3-25. The porous cup is buried in the soil and transmits the soil-water pressure to a pressure sensor. During normal operation, the saturated pores of the cup prevent bulk movement of soil gas into the cup. Water held by the soil particles is under tension; absolute pressure of the soil water is less than atmospheric. This pressure is transmitted through the saturated pores of the cup to the water inside the cup. Conventional fluid statics relates the pressure in the cup to the reading obtained at the manometer, vacuum gage, or pressure transducer, which are shown in Figure 3-26.

The tensiometers with water-filled tubes cannot be used at depths greater than approximately 5 to 7 m. This restriction arises because, in addition to the soil suction, a water column creates an extra negative pressure in the tensiometer, leading to the degassing of water and the accumulation of water vapor and air in the connecting tube extending to the surface. When the water pressure drops to -30 to -40 kPa, air nucleates in the tensiometer water and diffuses from the atmosphere and unsaturated soils through the connecting tubes and the ceramic tip, thus creating air bubbles. It is virtually impossible to avoid the formation of air bubbles even if deaerated water is used to fill the tensiometer. If the inner diameter of the tube is less than 4 to 5 mm, air may stick to the tube walls, gradually accumulate, and create air plugs along the water connecting tube. In tubes with larger diameters, air can move up and accumulate at the top of the tube. As the air volume increases, it forces

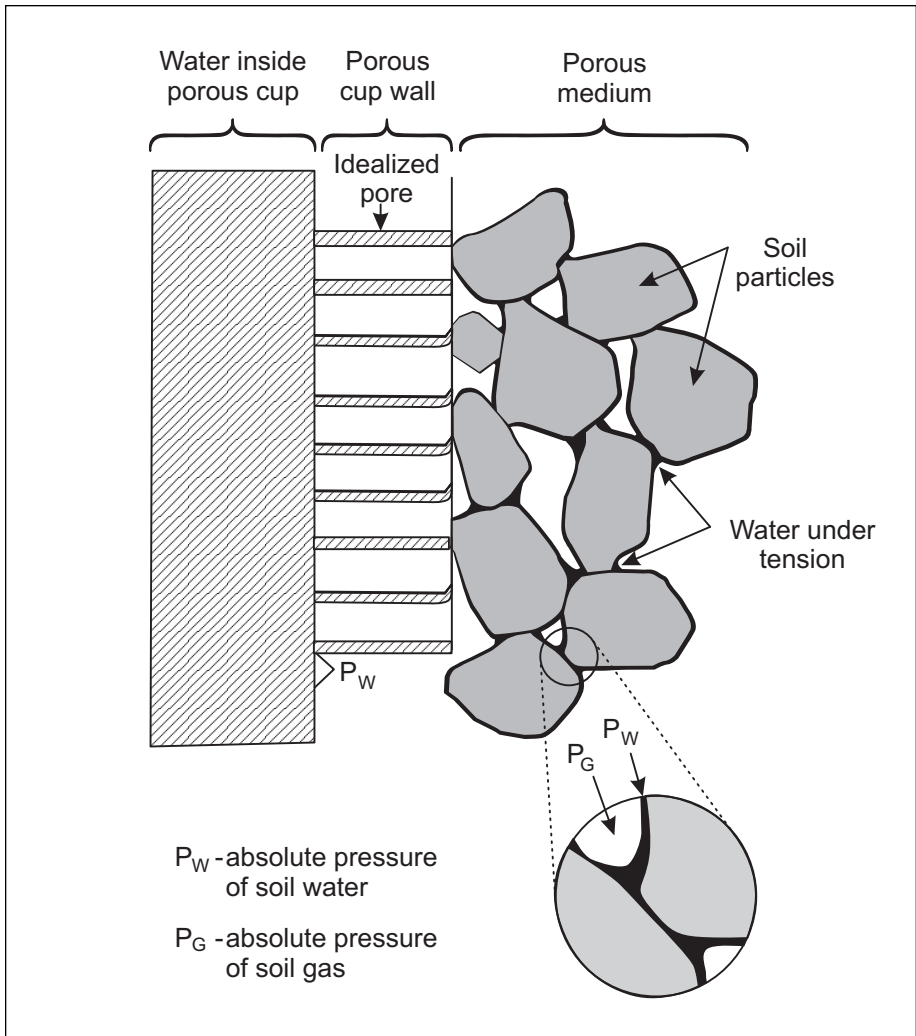


Figure 3-25. Enlarged cross section of porous cup-porous medium interface (ASTM, 1998)

water to discharge from the tensiometer into the surrounding soils, causing the water level in the water-filled tube to drop.

The porous tip of the tensiometer can have a cylindrical shape (Everett *et al.* 1984a), a conical shape (Dzekunov *et al.* 1987), or any other shape (for example, rectangular, ellipsoidal, circular or conical)

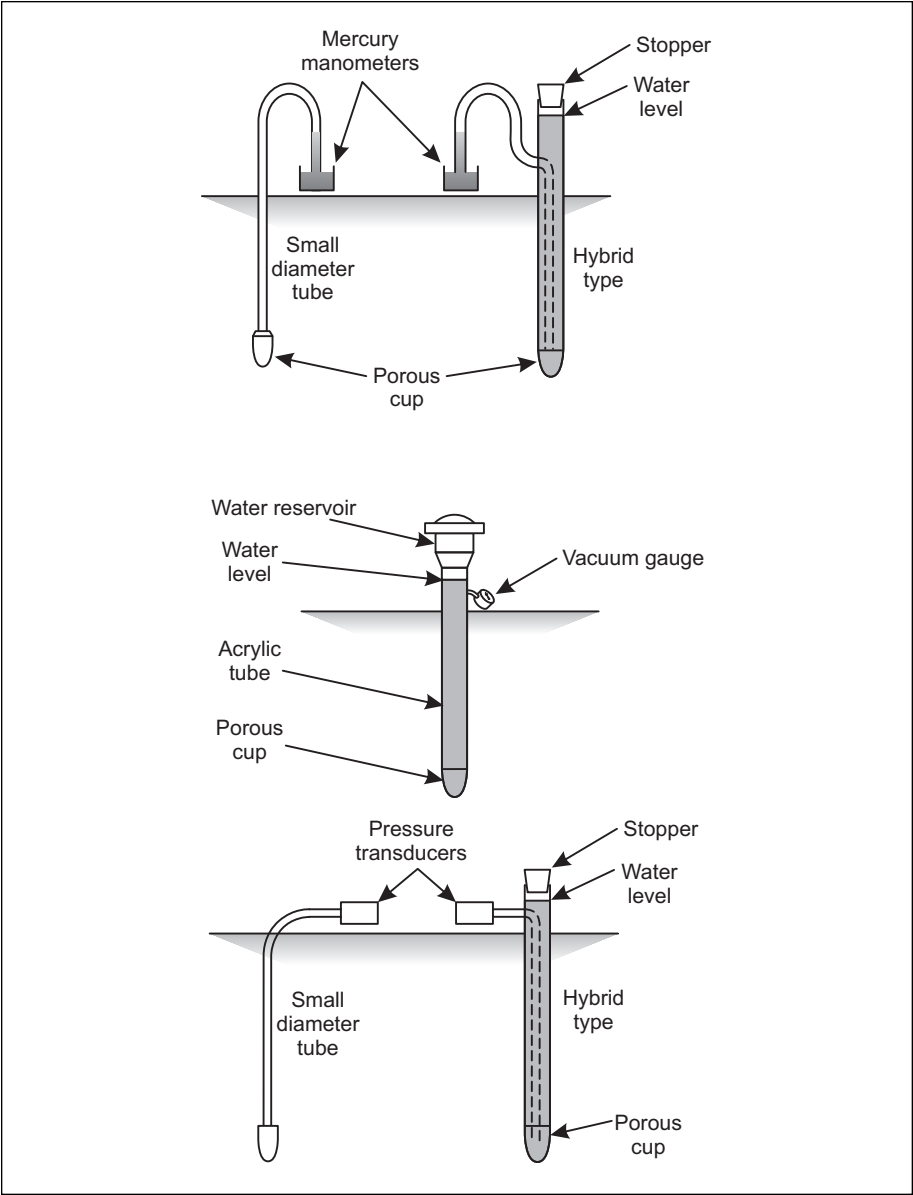


Figure 3-26. Three common types of tensiometers with different pressure sensors: (a) Manometer; (b) Vacuum Gage; and (c) Pressure Transducer (ASTM D 3404-91)

that enhances contact with the soil in a particular geological setting. For example, the upper portion of the tip may be cylindrical and the lower portion conical. The cylindrical portion of the porous tip maximizes surface contact with soil, whereas the conical shape may penetrate some soils more easily than the cylindrical shape, and thus create a better contact with soils. The cylindrical shape has been found advantageous in soft material, such as soil slurry, silica flour, or fine sand. The porous tip may be made from any water-permeable material that does not plug easily. Both ceramic material (for example, as fabricated by SoilMoisture Inc., of Santa Barbara, California) and stainless steel porous tubes (such as those manufactured by Soil Measurement Systems Inc., of Tucson, Arizona) can be used to make the tensiometer. Stainless construction of the porous tip is particularly useful when soils containing volatile organic compounds are to be investigated.

A better contact between the porous tip and surrounding soils can be achieved by inserting the tensiometer tip into a flexible, porous bag filled with soils taken during borehole drilling. Note that when the tensiometers are used to measure water pressure in contaminated soils, both the water and air may be mixed with impurities such as volatile organic compounds (VOCs), which may change the air pressure above the liquid level in the cells of the tensiometer.

Tensiometers can also be used for field measurements of water pressure in unfrozen soils at air temperatures below zero degree centigrade. In this application, the tensiometer cup and connecting tubes are filled in with an antifreeze solution (Gorden and Veneman 1995).

Problems with tensiometers designed for measuring water in the vadose zone include uncontrolled water-level changes when water from the soil enters the tensiometer, or when air enters the tensiometer and water discharges into the soils during soil drying.

Air-Free Tensiometers

In order to remove air accumulated in the tensiometer, Miller and Salehzadeh (1993) developed an air stripper. The stripper consists of an air-permeable tube that is inserted between the tensiometer fluid and a wet vacuum (containing some water droplets). When the vacuum is applied, air molecules diffuse from the tensiometer fluid into the stripper tube and are vented outside the tensiometer. By maintaining the wet

vacuum, the diffusion of water droplets from the tensiometer into the air stripper is practically eliminated. Ward *et al.* (1998) successfully coupled this method with time domain reflectometry (TDR) to obtain direct, continuous measurements of the matric potential in undisturbed cores, and then use the simultaneously determined moisture content and matrix potential to determine water retention curves.

Air-Pocket Tensiometer

Villa Nova *et al.* (1989) designed a tensiometer with an air pocket at the top of a water-filled tube connected to a porous tip. This tensiometer included only one tube, and the water level was required to be above the ground surface. Consequently, it was limited to measurement depths of approximately 5 m. If the water level in the tube were below the surface, it would vary in a manner that cannot be observed directly or controlled at the surface (Stephens 1996). Using the calculations of the volume of air above the water level based on Boyle's Law, Tokunaga (1992) determined the water level in a water-air access tube connected to a ceramic cup. In his apparatus, the same tube is used for both water and air feed.

Deep Tensiometers

Hubbell and Sisson (1998) developed an advanced tensiometer in which the porous tip is connected to a 1-in. polyvinyl chloride (PVC) tube through a central hole in the rubber stopper. The porous tip of the tensiometer is filled with water from the surface, and a pressure transducer is then lowered through the PVC access pipe and inserted into the rubber stopper hole. Thus, a water column between the tensiometer and the land surface was eliminated. However, this tensiometer has no control over the presence of water in the tensiometer. In order to either refill the porous cup with water or to check the tensiometer calibration, the pressure transducer (installed at the top of the porous cup) must be pulled to the surface. The total number of tensiometers installed in a single well is limited to the total cross-section of access pipes in this borehole. These tensiometers were tested under field conditions and showed good performance at several sites (Hubbell and Sisson 1998).

Morrison and Szecsody (1987) developed a solenoid transducer tensiometer that is installed at depths greater than 10 m and that automatically recirculates fluid at a given frequency (up to 42 days). However, like Hubbel and Sisson's model, this design has no control of the water level in the tensiometer. Therefore, the frequency of water replenishing is arbitrary.

Faybishenko (1999b) developed a two-cell tensiometer capable of (a) measuring water pressure in soils and rocks in the vadose zone and groundwater at any depth by measurement of a single parameter, namely, the pressure of an isolated volume of air in the tensiometer; and (b) maintaining a constant water level above the porous cup. Figure 3-27 depicts the design of the tensiometer. If the lower-cell water level drops below the bottom of the connector, water from the upper cell flows into the lower cell and reestablishes the water level in the lower cell. Thus, the lower cell maintains an essentially constant water level, above which a small air volume is isolated. Because the air volume in the lower cell is isolated, and because the lower-cell water-level height is kept essentially constant and is in equilibrium with the surrounding liquid, the pressure of the isolated lower air volume is directly proportional to the water pressure of the soil surrounding the porous tip of the tensiometer. Air pressure measured in both cells is stored remotely using a data acquisition system. The difference in pressure in both cells is used to determine the presence of water in the tensiometer. The tensiometer can be used in both drying and wetting conditions in the vadose zone and below the water table. Several tensiometers can be installed in a borehole at different depths to measure water pressure of soils or rocks above and below the groundwater table. The tensiometer can be used in both vertical and slanted boreholes with practically no limitations in depth. The tensiometer can also be designed as a suction lysimeter to collect water samples from surrounding soils. For this purpose, the water access tube may be extended to the bottom of the porous tip. Alternatively, a fourth tube can be used for this function.

Heat-Dissipation Method

The heat-dissipation probe is a small, porous, ceramic block containing a heater and a thermocouple embedded in a ceramic block (Reece 1996). The ceramic block is inserted in soils, and when a pulse of heat is applied to it, the thermal response is determined by measuring the volt-

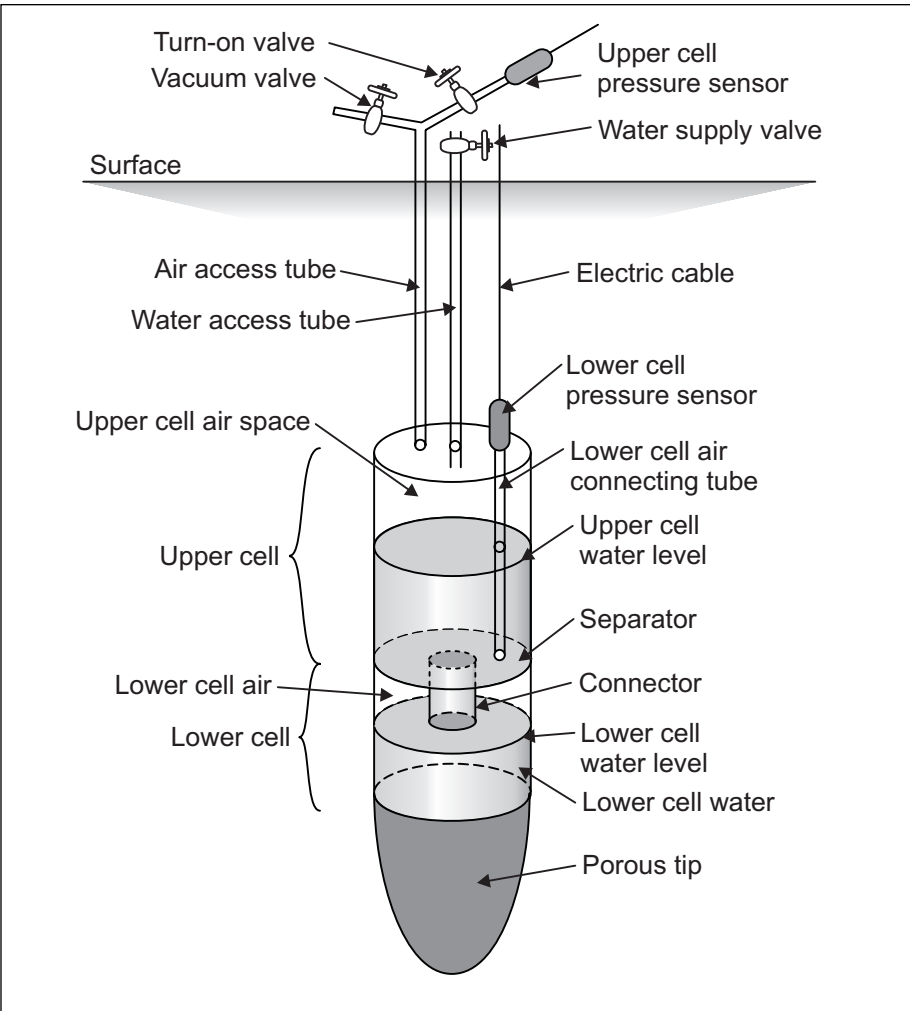


Figure 3-27. Schematic of the two-cell tensiometer (Faybishenko, 1999b).

age. This response is caused by heat dissipation, which is related to the water content of the ceramic block. It is assumed that the matric potentials of the ceramic block and the surrounding soils are in equilibrium. Therefore, if the heat dissipation probe is calibrated in terms of the matric potential, the soil matric potential can be determined. The practical range of the matric potential for the heat dissipation method is from the ceramic air entry value of about -0.1 bar to approximately -15 bar (Phene *et al.*

1992). A nearly linear relationship between the voltage and the matric potential exists in the range of -0.2 to -3.5 bar (Kutilek and Nielsen 1994). An advantage of the heat-dissipation probe over tensiometry is that water filling is not required, and therefore the system can operate in unsaturated soils with minimal maintenance. Heat-dissipation probes can also be connected to a data acquisition system. However, the heat-dissipation method does not work properly near the full water saturation and below the water table (if there is a need to determine the pressure distribution below the water table) because the analysis of the measurements is based on the assumption of a constant power dissipation (for all values of soil moisture content) at the heating element. The variations in the applied power may create temperature fluctuations, causing errors in the estimated matric potential (Bilskie 1999).

Granular Matrix Sensors

Electrical-resistance sensors (such as gypsum, nylon, or fiberglass matrix) for measuring matric suction (Eldredge *et al.* 1993, Shock *et al.* 1998) have not been very effective because of problems caused by salt effects, hysteresis, and degradation of the sensor material, particularly gypsum blocks (Campbell and Gee 1986). A new model of electrical-resistance sensors (WatermarkTM Irrometer Co., Riverside, CA) utilizes a gypsum block imbedded in a granular fill material. These new sensors have been used for agricultural applications. They were calibrated against neutron probes and tensiometers (Eldredge *et al.* 1993). The sensors were used in alkaline soils and were practically insensitive to low salt concentrations. However, they are temperature-sensitive, so that temperature corrections are required. The matric potential range of these sensors is from the air-entry value of granular material to about -10 bar or lower.

Filter-Paper Technique

The filter-paper method has been known for over 60 years, but its practical applications are limited. In this method, a small filter-paper disk is placed in contact with soil and is equilibrated for several days. The filter paper is then removed from the soil, and the water content of the filter paper is determined with a conventional gravimetric method. Using the known water-retention curve of the filter paper, the soil matric

potential is estimated. Advantages of this method include its simplicity, low cost, and its wide range of measurements (from near saturation to oven dry). The disadvantages are that the paper has to be removed from the soils and cannot be replaced at exactly the same location, and that a long equilibration time (up to a week or more) is needed for drier soils. Additionally, Deka *et al.* (1995), who compared the filter-paper method with tensiometry and psychrometry data, determined that for the dry materials, the filter-paper method overestimates the matric suction, because longer equilibrium times are required for drier samples.

Electro-Optical Methods

An electro-optical method can be used for measuring the water content of a filter paper (or any thin porous material, such as cellulose, nylon, or hydrophilic plastic filter paper) in a continuous fashion. Cary *et al.* (1991) developed a method of using a small light source, such as an infrared emitter, to beam light through the filter. The light is captured by a small photo-detector that measures output voltage as a characteristic of the attenuation of the light beam. The photo-detector voltage is a function of the water content of the filter. It is assumed that a unique, nonhysteresis relationship exists between the water content and matric suction of the filter. For dry soils, the method is insensitive to small changes in water content.

Thermocouple Psychrometry (TCP)

Comprehensive discussions on the use of TCP to measure soil-water potential and to estimate soil matric suction is provided by Rawlins and Campbell (1986) and Kutilek and Nielsen (1994). Thermocouple psychrometers infer the water potential of the soil liquid phase from measurements in the vapor phase. Use of thermocouple psychrometry for matric suction measurements is advantageous primarily in dry soils (-2 bar to -6 bar and lower). With TCPs, no direct hydraulic connection is required and only microscopic quantities of vapor are exchanged between soil and sensor. The main difficulty in using psychrometers arises because the range of the soil gas relative humidity is relatively narrow (from 0.99 to 1) in comparison to the wide range of the moisture content and water pressure (from 0 to -15 bar) for soils, which compli-

cates the calibration procedure of psychrometers. Andraski (1997) showed that although frequent calibrations of probes are required, TCPs could be used for at least five years.

Water Activity Meters

Chilled-mirror psychrometers (commercially available as water activity meters) have been used to measure total and matric soil suctions (Gee *et al.* 1992). Typically, these measurements are made under laboratory conditions on disturbed soil samples collected in the field with minimal water loss. The water activity meter can be used to estimate matric potential in soils with a low-salinity pore solution (less than 1 dS m^{-1}). Measurements in dry soils can be made quickly (in less than 5 minutes). A disadvantage of the water activity meter is that it becomes insensitive to changes in the matric potential (higher than -0.5 bar) in wet soils.

TDR-Tensiometer

An important innovation is the combination of a tensiometer and a TDR probe to obtain simultaneous measurements of the matric potential and moisture content of soils, which can be used to determine the water-retention curve under field conditions. In this method, tensiometer tips constructed from hollow metal tubes serve as the TDR wave guides. The TDR-tensiometer systems recently reported by Baumgartner *et al.* (1994) and Whalley *et al.* (1994) have two major differences. The Baumgartner *et al.* (1994) design shown in Figure 3-28 is based on a two-rod TDR system, which requires a balancing transformer. The tensiometer tubes are made of stainless steel tubes with porous steel cups welded or threaded to the distal end. In contrast, the Whalley *et al.* (1994) design is based on a three-rod TDR system with no balancing transformer. The tubes are made of aluminum, with porous ceramic cups glued to the distal end, and are filled with deaerated water. The tensiometer readings are taken using either a needle-tensiometer or a pressure transducer attached to the proximal end of each tube.

FIELD MEASUREMENTS OF WATER CONTENT IN UNSATURATED SOILS

One of the main goals of site characterization is to conduct rapid, reliable, and cost-effective monitoring of soil water content of soils needed

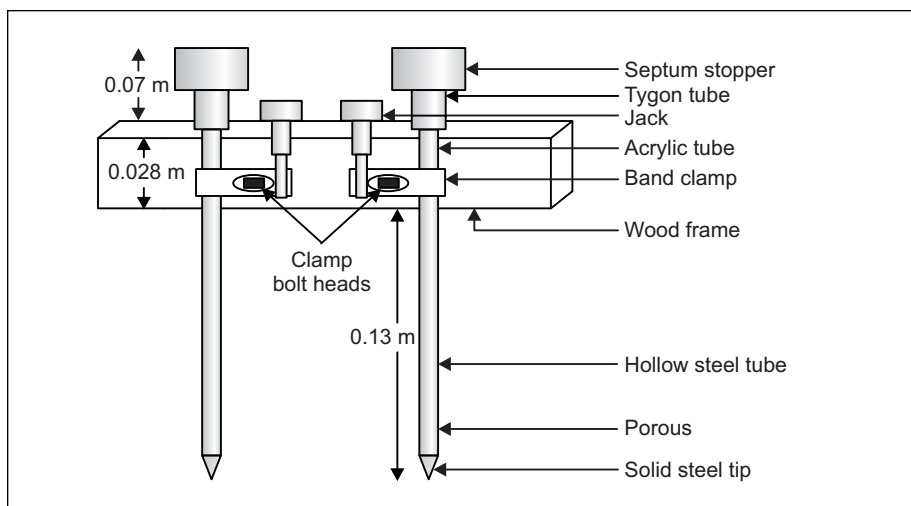


Figure 3-28. Schematic of a combination Tensiometer-TDR system
(Baumgartner *et al.* 1994)

in practically every aspect of site characterization. The moisture content, θ , along with the matric potential, ψ , are main parameters characterizing the spatial and temporal variations of water flow in the unsaturated-saturated soils and sediments of the vadose zone. These data are also used to estimate the main hydraulic parameters characterizing water flow, such as: the unsaturated hydraulic conductivity as a function of the water content $K(\theta)$; or the matric head, $K(\psi_m)$; or the water-retention function, $\theta(\psi_m)$, which is the relationship between the water content and matric potential.

Determination of the soil and sediment water content in soils and sediments can be conducted using direct and indirect methods. Direct methods involve removing water from a soil sample by evaporation, leaching, or chemical reactions, and measuring (or inferring) the amount of water removed (Gardner 1958). A key problem in water-content determination using direct methods is the difficulty in defining a dry soil, that is, determining when to stop water removal. This problem does not have a unique answer, because different soils are comprised of various amounts of colloidal and noncolloidal mineral particles, organic matter, volatile compounds, water, and dissolved chemicals. In particu-

lar, drying at temperatures in excess of 70°C can cause the decomposition of organic matter. On the other hand, soils with colloidal minerals may require temperatures between 165 and 175°C, while the standard range is 100 to 110°C. Examples of conventional direct methods of determining moisture content are gravimetry with oven drying, gravimetry with microwave oven drying, and alcohol leaching. Direct water-content measurements are destructive. Soil samples are taken at different places during borehole drilling.

Indirect methods of determining soil moisture content are based on measurements of some soil properties affected by water content, and are discussed next.

Neutron Logging

The neutron logging method is used extensively in soil sciences and civil and environmental engineering for determination of water content of soils, sediments, and rocks. The principle of neutron logging is based on the use of a radioactive source, such as americium-beryllium, that emits fast neutrons into the surrounding formation. The radioactive source is inserted in a borehole access tube, and neutron thermalization caused by hydrogen atoms in soil water and hydrocarbons is measured. The neutron logging procedure is approved by ASTM Standard D3017-96, and is described in detail in many texts and papers (such as Klute 1986; Jury *et al.* 1991; Kutilek and Nielsen 1994). A schematic of the neutron-logging principle is presented in Figure 3-29.

Neutron logging is a rapid and nondestructive method of *in situ* measurements in boreholes. It can be used for long-term, repetitive monitoring of the water balance and infiltration in the vadose zone.

The use of a neutron probe in environmental and environmental remediation applications usually requires a frequent recalibration of the neutron probe. This recalibration is necessary because of changes in the hydrogen concentration, especially in the presence of hydrocarbon contaminants. Neutron-probe measurements within the top 15 to 20 cm of the soil surface are not accurate because of neutron loss from the probe and the topsoil layer into the atmosphere.

The neutron logger provides measurements within the distance of 16 cm in wet soils to about 70 cm in dry soils (Kutilek and Nielsen 1994). Because the neutron logger is more sensitive to water near the

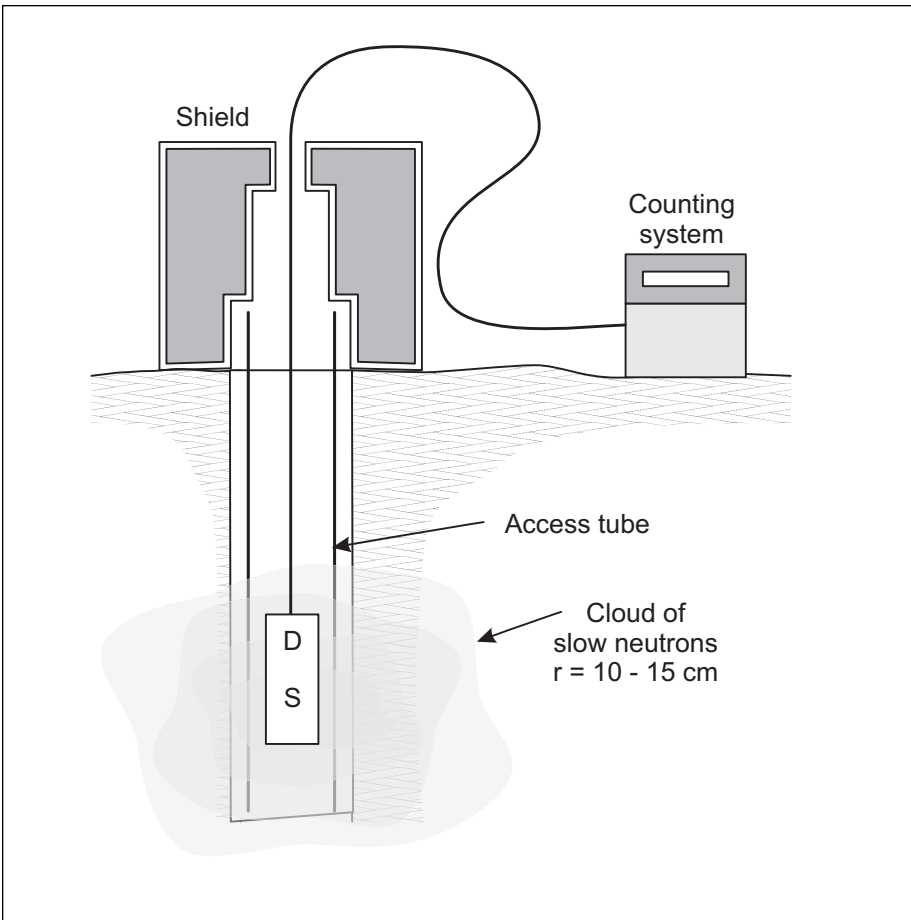


Figure 3-29. Schematic of a neutron probe used for measurement of soil water content in a soil profile (Kutilek and Nielsen 1994)

borehole than to water farther away, and because the soil volume involved in measurements varies as moisture content changes, the water content that is inferred from neutron logging is not a volume-averaged value. The low spatial resolution of neutron logging does not allow precise detection of changes in the moisture content caused by discontinuities in fractured rocks and heterogeneous soils. In addition, chemical composition, density, and heterogeneity of the formation may affect neutron-logging measurements.

The case study “Near Surface Infiltration Monitoring Using Neutron Moisture Logging, Yucca Mountain, Nevada,” by Alan L. Flint and Lorraine E. Flint, U.S. Geological Survey, describes a long-term monitoring program at Yucca Mountain. See page 457.



The calibration of neutron logging is needed to determine the absolute moisture content of soils. The calibration under field conditions is usually based on neutron logging with simultaneous sampling of soils to determine the moisture content by gravimetric method. The calibration under laboratory conditions involves measurements in large containers of soils with regulated moisture content. Laboratory calibration curves may be different from those obtained in the field because the soils in laboratory containers might have different textures than those under natural field conditions. The calibration curves may also depend on the neutron probe “aging” as well as the concentration of elements such as iron, boron, molybdenum, and cadmium. The errors of neutron logging can be reduced by determining the changes in the moisture content rather than the absolute values of the moisture content. The restrictions for using neutron probes require that the user have special training and a license for transport, ownership, and use of a radioactive source.

Time Domain Reflectometry Methods

General Considerations

The time domain reflectometry (TDR) technology has been employed successfully in geotechnical and mining industries for monitoring rock mass deformation and subsidence, and for measuring water level, water pressure, and soil moisture content (Huang and Dowding 1994; O’Connor and Wade 1994). The TDR method was first applied to soil-water investigations by Topp *et al.* (1980). This method is based on the determination of the propagation velocity of an electromagnetic wave along a transmission line (that is, waveguides inserted in the soil). Because of the large difference in dielectric constants of the soil components (Table 3-12), the TDR method is practically insensitive to soil solid-phase composition and texture. However, at contaminated sites, the dielectric constant may vary as the contaminant volume changes.

<div> <div>TABLE 3-12</div> <div>Dielectric Constants of Fluids and Solid Materials in the Range of Temperature from 20 to 25°C (CRC Handbook of Chemistry and Physics 1993; von-Hippel 1954)</div> </div>			
Fluids	Dielectric Constant	Solids	Dielectric Constant
Water	78.5 -80.4	Ice	3.7-4.1
Ethanol	24.3	Fused quartz (SiO ₂)	3.78
Acetone	20.7	Sandy soil (dry)	2.55
Ammonia	16.9	Loamy soil (dry)	2.51
Benzene	2.29	PVC	2.89
CO ₂ (liquid)	1.6	Polyethylene	2.2.5
CO ₂ (gas)	1.001	Teflon	2.1
Air	1.0	Wood	1.9–1.95

Two basic approaches have been used to establish the relationships between the soil-bulk dielectric constant (ϵ_b) and volumetric soil-water content (θ). The first approach is empirical and is based on fitting observed data of ϵ_b and θ using a polynomial function. Topp *et al.* (1980) described the observed relationship between ϵ_b and θ using a third-order polynomial given by:

$$\theta = -5.3 \times 10^{-2} + 2.29 \times 10^{-2} \epsilon_b - 5.5 \times 10^{-4} \epsilon_b^2 + 4.3 \times 10^{-6} \epsilon_b^3 \tag{3.2}$$

This equation describes the relationship $\epsilon_b(\theta)$ for the water content $\theta < 0.5$, with an error of approximately 0.013. However, this equation is not valid for soils with large concentrations of organic matter.

The second approach to describing the relationship $\epsilon_b(\theta)$ is based on assessing the contributions of dielectric constants of soil physical components, namely solid particles, gas, and water (Roth *et al.* 1990). According to Roth *et al.* (1990), a model for the bulk dielectric constant of a three-phase system is given by equation 3.3.

$$\epsilon_\beta = (\theta \epsilon_\omega^B + (1 - \phi) \epsilon_\sigma^B + (\phi - \theta) \epsilon_\alpha^B)^{(1/B)} \tag{3.3}$$

In this equation, ϕ is the soil porosity; B is an exponent that depends on the geometry of the medium in relation to the axial direction of the wave guide ($B = 1$ for an electric field parallel to soil layering, $B = -1$ for a perpendicular electrical field, and $B = 0.5$ for an isotropic two-phase mixed medium); $(1 - \phi)$, θ , and $(\phi - \theta)$ are the volume fractions of

solid, liquid, and gaseous phases; and ϵ_s , ϵ_w , and ϵ_a are the dielectric constants of the solid, liquid, and gaseous phases, respectively. Roth *et al.* (1990) showed that for $B = 0.5$, equation 3.3 produces a relationship similar to that of equation 3.2.

A variety of TDR probes were developed for different practical applications. Topp and Davis (1985) and Yokuda and Smith (1993) determined vertical moisture-content profiles using rods of different diameters at fixed intervals, which created impedance discontinuities. Ward *et al.* (1994) used horizontally installed probes. Ferre *et al.* (1994) developed a field multilevel probe consisting of two water-filled PVC access tubes (located in pilot holes) and a pair of target rods that are moved manually.

DeRyck *et al.* (1993) and Redman and DeRyck (1994) developed a multilevel TDR device that includes several horizontal rods attached every 2.5 cm to a PVC access tube at one end, and to a PVC support tube at the other. Each pair of rods forms a waveguide. A spring-loaded contact device moves through the access tube to provide measurements of changes in the apparent dielectric constant, which are related to changes in the moisture content. This approach was also used to determine the changes in concentration of kerosene and tetrachloroethylene (TCE). However, this technique was used only in repacked flow cells.

The assumption that the dielectric properties of soil water are similar to those of bulk water does not hold for sediments with high surface charge (Dirksen and Dasberg 1993; Roth 1990; White *et al.* 1992). Significant deviations from a linear calibration curve occur at low water contents because of the effect of bound water. Herkelrath *et al.* (1991) recommended determining the TDR calibration between ϵ_b and θ for particular types of soils investigated. The main advantages of the TDR method over other direct and indirect methods of soil-water content measurement are listed below:

- Accuracy may be up to 1 or 2 percent of the volumetric water content, if a proper calibration is made.
- Calibration may not be needed for non-saline soils.
- There are no radiation hazards associated with neutron-probe or gamma-attenuation techniques.

- TDR equipment (manufactured by Tektronix, Inc., and Campbell Scientific, Inc.) is available for telemetric and multiplexing enhancement of remote measurements in different geotechnical and environmental engineering applications (Huang and Dowding 1994).

Mallants *et al.* (1996) showed that the success or failure of TDR for monitoring solute transport depends on the quality of the calibration procedure. These authors recommended calibrating TDR probes using undisturbed soils taken from a location adjacent to the measurement point.

Bilskie (1999) showed that the error of the TDR method for measuring water content is caused by reflection distortion, which is caused either by attenuation in the coaxial connecting cables, or by attenuation of the signal at the probe via free ions in the soil solution. These processes are not taken into account in mathematical models used for evaluation of the reflection waveform. The TDR measurements can be improved by taking into account the resistance of the coaxial cable and connectors.

Remote-Shorting TDR Method

Hook *et al.* (1992) developed a remote-shortening method using a probe consisting of a conducting strip line, which is segmented using positive-intrinsic-negative diodes. Figure 3-30 shows a schematic of a seven-segment, eight-diode probe 1.85 m long that is used to monitor water storage in a hazardous-waste landfill cover at Hanford (Gee and Ward 1999). The diodes activated by the external voltage are used to apply a short circuit across the waveguides. A positive voltage shorts the first diode and opens the second diode. At the same time, a negative voltage reverses the process. It is assumed that the transit time of the electromagnetic (EM) pulse traveling along the segment is a linear function of the moisture content in this segment (Hook *et al.* 1992). Because this method is based on using the differencing technique, it can be used to obtain measurements with long cables and in saline soils.

Measurements at Hanford using cables 50 m long showed that the linear relationship between the water content and transit time holds for sands, however, it does not hold for silt loams, for which it becomes nonlinear (Gee and Ward 1999).

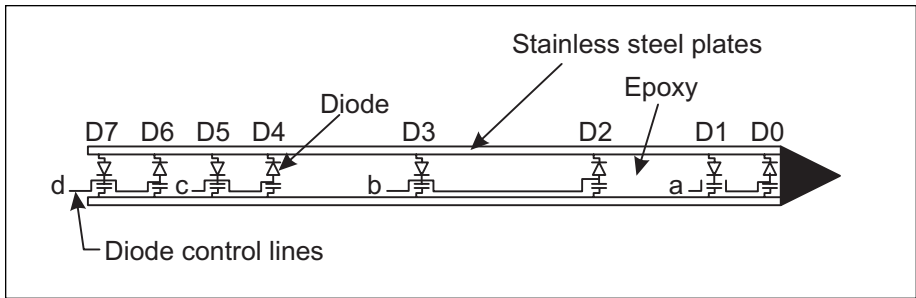


Figure 3-30. Schematic of a 7-segment, 8-diode probe, 1.85 m long with a 19x12.5 mm cross section. The space between the stainless steel plates is filled with electrical casting epoxy. The EM pulse generated by the TDR is introduced at diode D3 and propagates toward both ends. The diodes are switched with $\pm 5V$ DC using the control lines a, b, c, and d (Gee and Ward 1999)

To obtain small-scale, high-resolution TDR measurements, Nissen *et al.* (1999) proposed using a printed circuit board TDR probe that can increase the travel time of the electromagnetic waves in the waveguides.

TDR Measurements in Saline Soils

Dalton and van Genuchten (1986) determined that in saline soils with high bulk electrical-conductivity values, the attenuation of the TDR waveform leads to an overestimation of moisture content. To overcome this problem, Dalton and van Genuchten (1986) and Malicki and Skierucha (1989) proposed increasing the TDR voltage from the usual 250 mV.

Another approach to overcoming the problem of saline soils is the use of coated probes. These probes are now commercially available from most conventional TDR probe suppliers. Ward *et al.* (1992) tested TDR probes (coated with different nonconductive materials, namely, paint, epoxy resin, PVC heat-shrink tubing, ceramic, and a silicone-based compound) in high-salinity and high-temperature soils. The coated probes were tested in soil columns saturated with KCl solutions (0 to 0.4 M). Tests demonstrated that these probes can be used to determine travel time in soil under temperatures as high as 80°C. However, the disadvantage of coated probes is their variable sensitivity, which depends on the soil-moisture content (Ferre *et al.* 1998).

Ward *et al.* (1996) and Ward (1998) tested a prototype of a probe with waveguides 0.9 m long under laboratory and field conditions using the remote-shorting method and analyzed the results using a differential waveform analysis, which confirmed that this method is able to reliably measure transit time, dielectric constant, and electrical conductivity in saline soils.

Thermo-TDR Probe

The exchange of thermal energy in a soil is influenced by the soil-heat capacity and the thermal conductivity, both of which depend on moisture content. A thermo-TDR probe provides simultaneous measurements of the soil thermal properties and the bulk electrical conductivity. This probe combines a conventional TDR probe with a dual-heat-pulse probe (Noborio *et al.* 1996; Ren *et al.* 1999). The TDR probe comprises three hypodermic needles (20 gauge, 70 to 100 mm long) spaced 10 mm apart. A line heater and a thermocouple are enclosed in the center needle, and an additional thermocouple is located in one of the outer needles (Noborio *et al.* 1996). During the operation, the first step is to conduct a TDR probe measurement, and the second step is to apply heat to the center electrode (the heater) and to monitor the temperature in the outer electrode. Recorded TDR waveforms are used to determine the moisture content, while temperature measurements are used to calculate the thermal properties. Laboratory tests conducted for different soils in a range of the water content from 0.05 to 0.36 m³ m⁻³ showed that the probe provides quick, continuous, and accurate measurements of the soil thermal properties and water content. Field testing of this probe is needed. Because of the probe's small size, its application may be limited to non-consolidated soils into which it can be carefully installed.

TDR-Cone Penetrometer Method

A TDR-based moisture sensor was combined with the Navy's Site Characterization and Analysis Penetrometer System (SCAPS) to allow rapid, minimally-intrusive measurements of soil moisture content to depths of 45 m (Ward *et al.* 1996). In the first design, the TDR waveguide consisted of a pair of ring electrodes 2.5 cm thick and 40.6 mm in diameter that were electrically isolated from each other and from the steel mandrel using an ultra-high molecular-weight insulator. The probe was tested in the laboratory to obtain the correlation between the

moisture content and the dielectric constant. Several field tests were conducted to depths of 10 m at a coastal site in San Diego that was affected by seawater intrusion. To overcome problems caused by ionic solutes, Ward *et al.* (1996) and Ward (1998) used a helical waveguide with remote shorting and differential waveform analysis. The probe consisted of a pair of parallel stainless steel helices separated from each other and from the cone penetrometer mandrel by an insulator.

TDR-Tensiometer

A combination of a tensiometer with TDR probes, to obtain simultaneous measurements of the matric potential and moisture content of soils reported by Baumgartner *et al.* (1994) and Whalley *et al.* (1994), was described above. These probes were used in field-infiltration experiments by Si *et al.* (1999).

There are several vendors who manufacture TDR hardware. They are listed on the following Web site: <http://iti.acns.nwu.edu/clear/tdr/>.

Capacitance Methods

This borehole-logging method is based on using frequency-domain reflectometry (FDR) to determine the changes in the dielectric constant (capacitance) of a material. This method works well in homogeneous soils. Capacitance sensors have been used to measure soil-moisture content for many years (Thomas 1966; Dean *et al.* 1987). The results of measurements depend on the type of capacitance probe used. Evett and Steiner (1995) determined that a commercial probe (the Sentry 200 CP, developed by Troxler Electronics Laboratories, Raleigh, NC) produced a lower resolution in θ compared to the standard neutron-logging probe. Note that the soil volume for a capacitance probe is limited to a sphere of no more than a few centimeters around the probe access tube, which is considerably smaller than the sphere of influence of a neutron probe.

Paltineanu and Starr (1997) and Starr and Paltineanu (1998) successfully tested multisensor capacitance probes under laboratory and field conditions. The probes operate at a frequency in excess of 100 MHz (and are commercially available from EnviroSCAN, Sentek Pty. Ltd., South Australia).

Because the capacitance method uses a single-frequency approach, simultaneous measurement of soil temperature and the dielectric con-

stant allow one to determine the dielectric loss, which is needed to calculate the moisture content of saline soils (Hilhorst and Dirksen 1994). The response of FDR to changes in the moisture content is non-linear, and therefore, a careful calibration of the probes is necessary. This problem becomes more complex if the soil properties are changed over time, which may be the case for many environmental remediation sites. Under such conditions, the probes must be recalibrated.

Phase Transmission Methods (VIRRIB®method)

VIRRIB® method is based on measurements of the propagation of electromagnetic (EM) waves through the medium. This method was developed and successfully used for irrigation control and measurement of deep percolation in the Czech Republic (Litschmann 1991). Unlike TDR and capacitance methods, the VIRRIB method relies on the determination of a phase shift of a sinusoidal EM pulse, relative to the phase at the origin, after traveling a fixed distance along a conductor. According to Litschmann (1991), who extensively tested this method, the VIRRIB sensor consists of two stainless steel concentric circles (that must be inserted into the soil). These are connected in the body of the sensor, where the electronics are located. The sensor is embedded in a cover, which prevents water penetration into the electronic part. The diameter of the outer ring is 280 mm. The soil volume affected by measurements is approximately 15,000 to 20,000 cm³. The sensor uses DC current with a voltage of 12 to 20 volts supplied from an external source. The output current is directly proportional to the moisture content of the soils. Horizontally installed probes can measure the moisture content in a soil layer 12 cm thick, and vertically installed probes can measure the moisture content in a soil layer 30 cm thick. The primary advantage of these probes is that they can be connected to cables up to 1 km in length. However, very little data exist that document this promising method. Major disadvantages are the difficulty of installation of the sensor and its sensitivity to ionic solutes.

Electromagnetic Induction (EMI)

The spatial distribution of bulk electrical conductivity can be measured using Electromagnetic Induction (EMI) methods. Because a dry

soil layer is a poor conductor, the EM measurements depend on the water content, the solute concentration, and the amount and type of clay in the soil. Innovative applications of EMI for measuring water content were demonstrated for unsaturated soils (Kachanoski *et al.* 1988; Sheets and Hendrickx 1995), as well as radioactive sludges (Crowe and Wittekind 1995). Sheets and Hendrickx (1995) used a Geonics EM-31 ground-conductivity meter to monitor moisture content along a transect 1,950 m in length near Las Cruces, New Mexico. According to Sheets and Hendrickx (1995), changes in moisture content could be more accurately determined by changes in the EM measurements than by neutron logging. A disadvantage of this method is the ground-conductivity meter's sensitivity to metallic objects (such as fences, high-voltage power lines, and buried metallic objects), soil salinity, and temperature.

Thermal Probes

Campbell *et al.* (1991), Bristow *et al.* (1993), Tarara and Ham (1997), Bristow (1998), and Song *et al.* (1998, 1999) imposed changes in the temperature and thermal properties of soils, which are affected by the soil-moisture content. The probe used to affect these changes consists of two small needles separated a small distance, one of which is a heater, the other a thermal sensor. The heater periodically emits a pulse, and the thermal sensor needle monitors the temperature decay. The temperature decay is used to determine the soil volumetric heat capacity, which is a function of the soil-water content. Thermal probes are commercially available from Thermal Logic, Pullman, WA. The advantage of this method is that the probe is insensitive to the soil salinity. The main disadvantage is that only a small volume of soils is involved in measurements.

Fiber Optic Sensors

Fiber optic cables contain thin strands of glass that carry light. Fiber optic cables are lightweight and do not change the physical, chemical, or biological properties of soils. Moreover, they do not interfere with the electrical fields that may be generated by geophysical techniques. Fiber optic sensors are currently used in many scientific and industrial applications for real-time monitoring of a number of processes (Griffin and

Olsen 1992; Lieberman *et al.* 1990, 1991). The primary function of fiber optic sensors is to determine the changes that physical or chemical processes impose on a constant beam of light (Udd 1991). Fiber optic sensors have also found an application in environmental sciences (Lieberman *et al.* 1990; Rogers and Poziomek 1996).

Alessi and Prunty (1985) determined the moisture content of soils by measuring the attenuation of light transmitted through an optical fiber embedded in soil. The light received from the sensor was converted to a voltage. The resulting measurements showed a linear relationship between the voltage and the moisture content of a silt loam soil. An important advantage of this method is its independence of the salinity of soils.

According to the DOE Characterization, Monitoring, and Sensor Technology-Cross-Cutting (CMST) Program, the design, construction, and evaluation of fiber optic, laser-induced breakdown spectroscopy (LIBS) probes in conjunction with a cone penetrometer are in progress at Science and Engineering Associates, Inc. (Stephen Saggese, Principal Investigator). The purpose of these instruments is to quantify the concentration of heavy metals such as Cr, Pb, and other DOE-specified elements. Sandia National Laboratories is fabricating, testing, and evaluating a new cone penetrometer for characterizing hydrogeologic parameters and subsurface contaminant concentrations with fiber optic probes and a Time Domain Reflectometry (TDR) sensor.

CHEMICAL DISTRIBUTION AND TRANSPORT MONITORING

Monitoring of chemical transport in the vadose zone involves determining the concentration of chemicals in the pore liquid. Various types of pore-liquid samplers were discussed by Morrison (1983), Wilson (1980, 1981, 1982, 1983, 1990), Everett (1981), Everett *et al.* (1982, 1984), Robbins and Gemmel (1985), Merry and Palmer (1986), U.S. EPA (1986), and Ball (1986).

Suction Lysimeters*

*This section was contributed by L. Everett and B. Faybishenko.

Suction lysimeters are devices that are used for collecting pore-liquid samples from unsaturated and saturated soils and fractured rocks. The description of suction lysimeters is given below based on recommendations summarized in the ASTM D 4696-92 Standard Guide.

The selection of the sampler type for site characterization and monitoring should be based on consideration of several criteria, including sampling depths and required sample volumes for a particular type of analysis (volatile organic compounds [VOCs], major ions, or radioactive elements). Table 3-13 summarizes the features of various types of suction samplers.

Vacuum lysimeters are samplers that can be used at depths up to 6 or 7.5 m. *Pressure-vacuum lysimeters* are samplers that can be used at depths up to 10 or 15 m. *High-pressure-vacuum lysimeters* (also known as pressure-vacuum lysimeters with transfer vessels) can be used from the surface to depths at least 91 m. (Installations as deep as 91 m were reported by Bond and Rouse [1985].) *Suction lysimeters with low bubbling pressures* can be used to maximum depths from about 7.5 to 46 m (U.S. EPA 1986; Johnson and Cartwright 1980).

Suction lysimeters consist of a hollow porous tip attached to a vessel or a body tube. Samples are obtained by applying a vacuum to the sampler and collecting pore-liquid in the body tube (Figure 3-31). When suction greater than the soil pore-liquid capillary pressure is applied to the sampler, liquid moves into the sampler. Ceramic porous segments are hydrophilic, and the maximum pore sizes are small enough to allow menisci to withstand the entire range of sampling suctions. If the maximum pore sizes are too large, the menisci are not able to withstand the applied suction. When the menisci break down, hydraulic contact between the water in the porous tip and soils is lost, and soil air enters the sampler, leading to the release of suction.

There are several methods for retrieving liquid collected in the sampler. For depths up to 6 or 7.5 m, liquid samples can be brought up to the surface using suction (Figure 3-31a). For depths greater than 6 or 7.5 m, samples may be retrieved by pressurizing the gas above the liquid in the sampler through a gas-access line, which pushes the liquid sample up to the surface through a second line (Figure 3-31b).

Pressure-vacuum lysimeters (Parizek and Lane 1970) for deep sampling (Figure 3-31b) have two lines that are forced through a two-hole stopper sealed into the upper end of the body tube. The discharge line

TABLE 3-13 Suction Sampler Summary (ASTM D 4696-92)

Sampler Type	Porous Section Material	Maximum^A Pore Size (μm)	Air Entry Value (cbar)	Operational Suction Range (cbar)	Maximum Operation Depth (m)
Vacuum lysimeters	Ceramic	1.2 to 3.0 (1) ^A	>100	<60 to 80	<7.5
	PTFE	15 to 30 (2) ^A	10 to 21	<10 to 21	<7.5
	Stainless steel	NA ^B	49 to 5	49 to 5	<7.5
Pressure-vacuum lysimeters	Ceramic	1.2 to 3.0 (1) ^A	>100	<60 to 80	<15
	PTFE	15 to 30 (2) ^A	10 to 21	<10 to 21	<15
High pressure-vacuum lysimeters	Ceramic	1.2 to 3.0 (1) ^A	>100	<60 to 80	<91
	PTFE	15 to 30 (2) ^A	10 to 21	<10 to 21	<91
Filter tip samplers	Polyethylene	NA ^B	NA ^B	NA ^B	None
	Ceramic	2 to 3 (1)	>100	<60 to 80	<7.5
	Stainless steel	NA ^B	NA ^B	NA ^B	None
Cellulose-acetate hollow-fiber samplers	Cellulose Acetate	<2.8	>100	<60 to 80	<7.5
	Non cellulosic Polymer	<2.8	>100	<60 to 80	<7.5
Membrane filter samplers	Cellulose Acetate	<2.8	>100	<60 to 80	<7.5
	PTFE	2 to 5	NA ^B	NA ^B	<7.5
Vacuum plate	Alundum	NA ^B	NA ^B	NA ^B	<7.5
	Ceramic	1.2 to 3.0	>100	60 to 80	<7.5
	Fritted glass	4 to 5.5	NA ^B	NA ^B	<7.5
	Stainless steel	NA ^B	49 to 5	49 to 5	<7.5

^APore size determined by bubbling pressure (1) or mercury intrusion (2).

^BNA = Not available

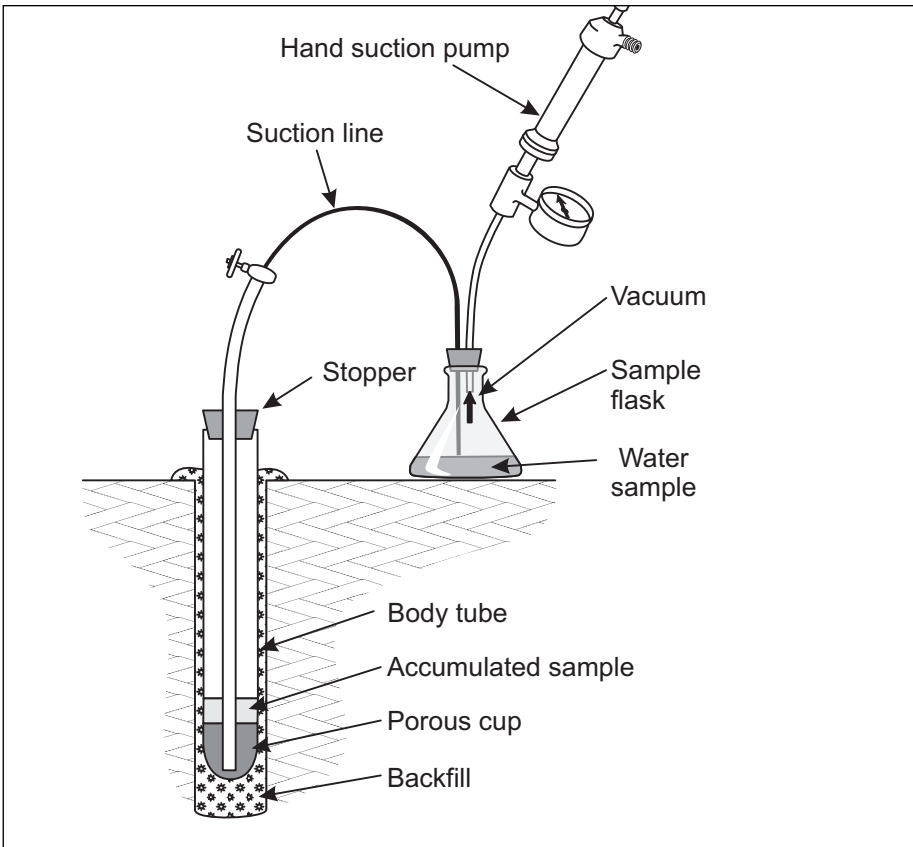


Figure 3-31a. Schematic of vacuum lysimeter (ASTM D 4696-92)

extends to the base of the sampler, and the pressure-vacuum line terminates just below the top stopper. At the surface, the discharge line connects to a sample bottle and the pressure-vacuum line to a pressure-vacuum pump. These samplers can retrieve samples from depths greater than 7.5 m because pressure is used to retrieve liquid samples. During pressurization, however, some of the sample is forced back out of the cup. At depths greater than 15 m, the volume of sample lost in this fashion may be significant. In addition, at these depths, pressures required to bring the sample to the surface may be high enough to damage the cup or to reduce its hydraulic contact with the soil (Young 1985).

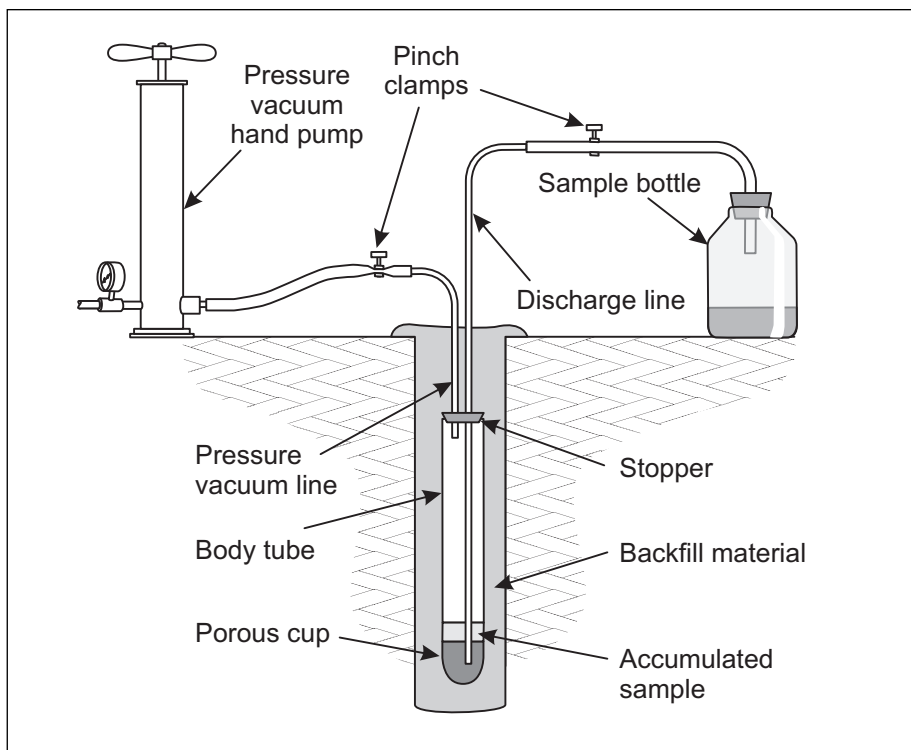


Figure 3-31b. Schematic of pressure vacuum-lysimeter (ASTM D 4696-92)

High-pressure-vacuum lysimeters operate in the same manner as pressure-vacuum lysimeters. These instruments include a built-in check valve between the chambers, which prevents both sample loss through the porous tip during pressurization, and possible cup damage caused by over-pressurization.

Filter-tip samplers consist of two components: a permanently installed filter tip, and a retrievable glass sample vial. The filter tip includes a pointed end to help with installation, a porous section, a nozzle, and a septum. The tip is threaded onto extension pipes that extend to the surface. The sample vial has a second septum, and when in use, the vial is seated in an adaptor with a disposable hypodermic needle. The needle penetrates both septa, allowing the sample to flow from the porous segment into the vial. The inside diameter of the extension pipes varies from 2.5 to 5.1 cm. Vial volumes range from 35 to 500 mL.

(Knighton *et al.* 1981). The body of the filter tip is made of thermoplastic, stainless steel, or brass, and the attached porous tip is constructed from either high-density polyethylene, sintered ceramic, or sintered stainless steel. The septum is made of natural rubber, nitrile rubber, or fluororubber (Knighton *et al.* 1981). Filter-tip samplers collect liquid samples by lowering an air-evacuated sample vial through an access tube to a permanently installed porous tip. The vial is connected to the porous tip, liquid flows from the porous tip into the vial, and the vial is then retrieved.

Various materials have been used for the porous tip, including nylon mesh (Quin and Forsythe 1976), fritted glass (Long 1978), sintered glass (Starr 1985), stainless steel (Mott Metallurgical Corp. 1988), and ceramics (SoilMoisture Equipment Corp. 1988). The sampler body tube has been constructed with PVC, acrylic, and stainless steel (Smith *et al.* 1986; Caster and Timmons 1988; SoilMoisture Equipment Corp. 1988).

A cellulose-acetate, hollow-fiber sampler (Jackson 1976; Wilson 1981) consists of a bundle of flexible, hollow fibers (maximum pore size of less than 2.8 μm) pinched shut at one end and attached to a suction line at the other end. The suction line leads to the surface and attaches to a sample bottle and the source of suction in the same manner as a vacuum lysimeter. The fibers, which are analogous to the porous sections of vacuum lysimeters, have outside diameters of up to 250 μm (Levin and Jackson 1997). Levin and Jackson (1977) described similar fibers made from a noncellulosic polymer solution (maximum pore size of less than 2.8 μm). Those fibers have dense inner layers surrounded by open-celled, spongy layers with diameters ranging from 50 to 250 μm .

A membrane-filter sampler (Stevenson 1978; Morrison 1983; Everett *et al.* 1982; U.S. EPA 1986) consists of a membrane filter of polycarbonate, cellulose acetate (maximum pore size of less than 2.8 μm), or cellulose nitrate, that is mounted in a “swinnex” type filter holder (Stevenson 1978; Wagemann *et al.* 1974; Wilson 1983). The filter rests on a glass fiber prefilter, the prefilter on a glass fiber “wick,” and the glass fiber “wick” on a glass fiber collector. The collector is in contact with the soil and extends the sampling area of the small-diameter filter. A suction line leads from the filter holder to the surface. At the surface, the suction line is attached to a sample bottle and the suction source in a manner similar to vacuum lysimeters.

To reduce chemical interference from substances on the porous tips, the U.S. EPA (1986) recommended preparation of ceramic units prior to installation, following procedures originally developed by Wolff (1967), Wood (1973), and Neary and Tomassini (1985). The process involves passing hydrochloric acid (HCl) through a porous tip.

Morrison and Szecsody (1985) found that the radius of sampling influence is maximized if the borehole diameter is only slightly larger than that of the sampler, and if a silica flour pack is used. The U.S. EPA (1986) recommended that the hole have a diameter at least 5 cm larger than the sampler, which will facilitate installation of the silica flour. The silica flour slurry is usually emplaced using the tremie-pipe method. The excess water from the sampler and silica slurry should be removed immediately after installation (U.S. EPA 1986). To allow the samplers to equilibrate with the surrounding soil, Litaor (1988) recommended their installation a year before sampling begins.

Cellulose-acetate hollow-fiber-sampler installation procedures were described by Everett *et al.* (1984); membrane-filter-sampler installation procedures were described by Stevenson (1978), Everett *et al.* (1984), and Morrison (1983); and vacuum-plate-sampler installation procedures were described by Everett *et al.* (1984) and Morrison (1983). Because the fibers are thin and fragile, to be positioned in the soil, they must be placed in a predrilled vertical or horizontal hole or installed in a perforated, protective PVC tubing filled with soil slurry (Silkworth and Grigal 1981).

Membrane-filter samplers are placed in a hole to the top of the selected sampling depth. First, sheets of the glass fiber "collectors" are placed at the bottom of the hole. These collectors develop the necessary hydraulic contact between the sampler and the soil, and because they cover a larger area than the filter holder alone, they also extend the area of sampling. Second, two or three smaller discs are placed on the collectors. Third, the filter holder fitted with a glass fiber prefilter and the membrane filter is placed on top of the wick disks. The suction line leads to the surface. Finally, the hole is backfilled (Morrison 1983; Everett *et al.* 1984).

The major causes of sampler failure are line damage and leaks (caused by freezing, installation, rodents, and so on), connection leaks, and clogging of the porous material. Freeze damage to the lines can be minimized if the lines are emptied of sample prior to applying a vacuum. Care must be taken to prevent the tubing line from freezing.

Biofilm growth and plugging by colloids may clog porous tips (Morrison 1983; Quin *et al.* 1976; Debyle *et al.* 1988). However, such clogging may not affect the composition of liquid sampled, but will may only increase the time of sampling (U.S. EPA 1986; Johnson and Cartwright 1980).

Morrison and Szecsody (1987) described devices that could be used as tensiometers and then converted to pressure-vacuum lysimeters. However, they found that gases entering these devices prevented accurate measurement of pore-liquid tensions. Baier *et al.* (1983) also discussed methods of converting tensiometers to pressure-vacuum lysimeters. Suction lysimeters may be used as tensiometers, but the volume of water drawn from the soil through a lysimeter may significantly affect natural pore-liquid tensions (Taylor and Ashcroft 1972).

Operational lifetimes of suction samplers depend on installation, subsurface conditions, maintenance, and sampling frequency. Some samplers are operational for as long as 25 years (Baier *et al.* 1983).

Because vacuum lysimeters and experimental samplers use suction to retrieve samples, the maximum sampling depth is limited by the maximum suction lift of water, about 7.5 m (U.S. EPA 1986). In practice, these samplers are generally used to approximately 2 m below the surface (U.S. EPA 1986). They are primarily utilized to monitor near-surface movement of pollutants, such as those from land disposal facilities or from irrigation return flow.

Ordinarily, pressure-vacuum lysimeters are not used deeper than 15 m below ground surface. At greater depths, sample loss and overpressurization problems are considered significant enough to warrant the use of high pressure-vacuum lysimeters that do not have these limitations. High-pressure-vacuum lysimeters are not preferred at shallower depths because they are more expensive than pressure-vacuum lysimeters. In addition, high-pressure-vacuum units have more moving parts than pressure-vacuum units, and as a result, the possibility of failure is higher.

Factors affecting the volume of a pore-liquid sample are the suction applied, the schedule of suction application, the spatial distribution of pore-liquid, the soil texture and structure, and the porous tip design. Samples collected with lower suctions (approximately 10 cbar or less) usually come from liquids migrating through soil macropores (Morrison 1983). Samples collected with higher suctions (greater than about 10 cbar) also include fluids held at higher tensions in micropores. The case

"Characterization and Monitoring of Unsaturated Flow and Transport Processes in Structured Soils," by Philip M. Jardine, R.J. Luxmoore, J.P. Gwo, and G.V. Wilson, illustrates the application of liquid samplers with different suctions. See page 473.



study illustrates the application of liquid samplers with different suctions.

The sampler may disrupt normal flow patterns as a result of the applied suctions. Although the area nearest the sampler undergoes the most disturbance, the effects may extend several meters from the sampler (Bouma *et al.* 1979; Warrick and Amoozegar-Fard 1977; Van der Ploeg and Beese 1977). Because of this disturbance, samples are averages of the affected flow area rather than point samples (Morrison 1983). Morrison and Szecsody (1985) found that (under the conditions of their study) the radii of influence for suction lysimeters ranged from 10 cm in coarse soils up to 92 cm in fine-grained soils.

Sampling with falling suction produces samples with compositions that are "averages" of the liquids held at the range of tensions applied. Because suctions, and, therefore, inflow rates, decrease with time, these "averages" are weighted toward the portions of the samples obtained in early times. Samples collected over prolonged periods are "averages" of the liquids flowing past the sampling region.

During wet periods, samplers affect a small volume of soil and pull liquids from a sequence of pores that may include macropores. During dry periods, samplers affect a larger volume of soil, draw from micropores (because the macropores have been drained), and collect less liquid (Anderson 1986). The net result of these trends is that sampled soil solutions are "averaged" over different volumes and derived from different pores as a function of the soil-moisture content and distribution.

Soil textures and pore-liquid tensions control a sampler's radius of influence, and the amount of liquid that it can remove. The slope of the pore-liquid release curve for a sand is greater than that for a clay at low pore-liquid tensions. This indicates that, for an equal change of pore-liquid tension at these low tensions, a larger quantity of pore-liquid will be released from a sand than from a clay. At higher tensions, the slope of a clay pore-liquid-release curve is greater than that of sand. This indicates that more pore-liquid will be released from a clay than from a sand

for an equal change in pore-liquid tension at higher tensions. Therefore, suction samplers may not obtain samples from coarse-grained soils at higher pore-liquid tensions.

Hansen and Harris (1975) demonstrated that intake rates may vary substantially because of variability in the ceramic sections from one manufacturer's batch to another. The intake rate of a sampler is also a function of the degree of clogging. The range of pore-liquid tensions over which a sampler can operate is a direct function of the maximum pore size of the porous section.

Nagpal (1982) recommended that several consecutive extractions of liquids be taken during a sampling event, and that only the sample from the last extraction be used for chemical analyses. The purpose of this is to flush out cross contaminants from previous sampling periods, and to ensure that any porous segment/soil solution interactions have reached equilibrium. Debye *et al.* (1988) also suggested discarding the first one or two sample volumes when sampling dilute solutions with newly flushed (HCl method) and installed samplers. The purpose of this is to allow the cation exchange between the porous segment and the pore-liquid (caused by the HCl flushing) to equilibrate.

Other Methods

Electrical-Conductivity Imaging

Electromagnetic-conductivity imaging is a relatively rapid and cost-effective field method to investigate the spatial and temporal variability in soil salinity, and it is widely used all over the world. Several field tools were developed (GEONICS EM31, EM34, EM38) that replaced the traditional four-electrode resistivity traversing techniques. The advantage of electromagnetic-induction tools is that ground-contacting electrodes are not required, and consequently, these tools can be used in open boreholes in the vadose zone. Williams and Baker (1982) showed that EM meters can be used for measurements in saline soils. To provide measurements in saline soils, Rhoades and Oster (1986), Cook and Walker (1992), and Acworth (1999) determined the empirical correlation between the soil salinity and the measured electrical conductivity (EC). The EC of a homogeneous porous material depends on many variables, including porosity, saturation, clay content, grain size, and the total dissolved solids in the soil water.

Using inversion, a two-dimensional vertical section of true electrical conductivity can be created from field images of apparent electrical conductivity (Acworth 1999). The distribution of different electrical-conductivity zones can be correlated against borehole and other field data.

Fiber Optics

Ghodrati (1999) developed a method for and demonstrated successful applications of the fiber optic sensors for *in situ* point-type measurements of the breakthrough curves. (The description of the principle of fiber optics is given in the section “Field Measurements of Water Content in Unsaturated Soils,” above).

TDR Probes

TDR probes that were initially designed to measure moisture content also can be used to determine breakthrough curves. There are numerous examples showing the performance of TDR probes to monitor the chemical transport. (The description of the performance of TDR probes in saline soils is given in the section “Field Measurements of Water Content in Unsaturated Soils,” above).

Pore Water Extraction by Refractometer

Soil pore solution can be extracted using the refractometer method. Pore water is squeezed from fine-grained soil samples (ASTM D 4542-95 Standard Test Method) and this water is used to determine the soluble chemicals in the extracted pore water. This method is applicable for soils with water content equal to or greater than approximately 14 percent, by volume. An extensive summary of methods used to extract pore water from soils has been presented by Kriukov and Manheim (1982). The refractometer method cannot be used to extract liquids from coarse-grained soils, such as sand or gravel.

SEAMIST Absorbent Pads

Soil pore solution of low-moisture-content soils can be extracted using absorbent pads attached to the outside surface of SEAMIST liners, which are pressed against the walls of the borehole. (See the section “Removable SEAMIST™ Liners,” above for the details of installation.)

SOIL GAS CHARACTERIZATION AND MONITORING

Goals of Soil-Gas Monitoring

Soil-gas monitoring is a widely used and effective method of subsurface investigations in several industries, including agriculture (Boynton and Reuther 1938), petroleum and mineral exploration (Horvitz 1969; Ullom 1988), underground coal gasification (Jones and Thune 1982), and environmental investigations (Roffman *et al.* 1985; Wittmann *et al.* 1985). Soil-gas monitoring is used to assess the extent of groundwater contamination by volatile organic contaminants (Wittmann *et al.* 1985), and to detect discharges to the vadose zone and groundwater from underground storage tanks (Scheinfeld and Schwendeman 1985; Wittmann *et al.* 1985). The RCRA and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) recommend soil-gas monitoring for soil and groundwater remedial actions (Karably and Babcock 1989).

In addition to measuring the soil-gas concentration along the soil profile, there is a need to measure soil gas flux, especially at the soil surface (Rolston 1986). These measurements are conducted to assess the soil-atmosphere gas exchange and to determine, directly, the gas flux. One of the methods developed for this purpose is the use of closed chambers installed over the soil surface.

It is important to note that soil-gas monitoring cannot be used as a stand-alone method, but only in combination with other methods. The success of soil-gas monitoring is strongly dependent upon the effects of geologic variation and moisture content in the sampling horizon, as well as the physical properties of contaminants. Note also that the soil gas sampled actually represents a mixture of soil gas and atmospheric air entering the soil at the time of sampling. Atmospheric air can enter soils through macroporous or soil cracks, which are located far from the sampling device.

Soil-Gas Characterization and Monitoring for VOCs*

Soil-Gas Processes Affecting VOC Concentrations

*This section was contributed by L. Everett and B. Faybishenko.

Soil-gas processes and monitoring methods are described below using the ASTM Standard 5314-92. The soil-gas composition depends on a combination of several processes, such as migration, partitioning, and degradation of chemicals. Chemicals can enter the soils either in the liquid or vapor phase from the surface, from groundwater, or from leaking underground tanks (see Chapter 1).

Partitioning is the process that controls contaminant movement between phases. The unsaturated zone has four phases of interest: the water phase, the soil mineral and organic particle phase, the gas phase, and the nonaqueous phase liquid (NAPL) phase. In unsaturated soils, partitioning depends on air-filled porosity, water content, the presence and composition of NAPL, and the presence of clay and discrete inorganic soil particles.

Partitioning includes dissolution, adsorption, volatilization and evaporation. Dissolution is the partitioning of contaminants between the NAPL and water phases. It is impacted by the presence of liquid-phase co-solvents (such as gasoline additives) even at low concentrations in liquid-phase mixtures. The change in dissolution equilibrium can affect certain liquid-phase components in water, often enhancing the solubility of the components beyond what is indicated by partitioning coefficient data generated under laboratory conditions.

The effects of temperature upon dissolution are generally insignificant for aliphatic hydrocarbons between 15 and 50°C (Price 1976), which is typical for most vadose zone soils under natural conditions. However, temperature effects upon dissolution equilibrium can be significant for other contaminants (Owens *et al.* 1986). Dissolution equilibrium is also affected by changes in water salinity. The rate of dissolution depends upon the partitioning coefficient of the particular contaminant of interest and the degree to which the NAPL phase and water have been mixed. For example, frequent water-level fluctuations accelerate partitioning contaminants accumulated within the capillary fringe.

Volatilization and evaporation are the processes of evaporating volatile contaminants moving from either the NAPL or the liquid phase water phase to the surrounding gas phase. However, the soil-gas composition may not be similar to that of the liquid phase, because of the lack of constituents with the lowest vapor pressures. The rate of volatilization is expected to be higher in macroporous soils as affected by soil-gas convection currents. Manos *et al.* (1985) demonstrated that

the organic matter and clay content in the soil impact the volatile organic-compound emission from soils. Soil-gas contaminants with high sorption properties cannot be efficiently sampled. Knowledge of the presence of barriers to vertical or horizontal migration (such as foundations, buried pavement, or perched water zones) and the existence of preferential pathways for contaminant migration (such as backfill rubble, utility vaults, storm sewers, or soil cracks) can assist in designing the soil-gas monitoring system.

Degradation is the process of contaminant attenuation by oxidation or reduction, either through biogenic or abiogenic processes. Degradation by oxidation usually occurs in shallow soils. Biodegradation is caused by the presence of microorganisms capable of using the contaminant as a substrate. Populations of various microorganisms that naturally occur in soils can degrade petroleum products (Dragun 1985). Contaminant biodegradation is known to occur in groundwater and in soils prior to contaminant partitioning into a vapor phase (Davis 1969). Contaminant biodegradation rates are highly variable and are controlled by a number of kinetic factors influencing the distribution of microorganisms (White *et al.* 1985; Jensen *et al.* 1985).

Contaminants can degrade to compounds that may or may not be detectable in soil gas. For example, while aerobic degradation can produce carbon dioxide, which is easily detectable and is an indirect indicator of the presence of contaminants (Diem *et al.* 1987), this process can also generate organic acids and phenols (Dragun 1985), which are not routinely detectable using whole-air soil-gas sampling because of their low Henry's constants. Anaerobic degradation can produce compounds such as methane, ethylene, propylene, acetylene, and vinyl chloride, which also can be monitored as indirect indicators of the presence of contaminants.

Biodegradation of contaminants in the vadose zone can also occur naturally. Natural biodegradation can result from indigenous microbial populations adapting to metabolize contaminants as primary substrate, or by introducing foreign populations that have been preconditioned to metabolize contaminants of interest. Certain compounds may not be present in soil gas because of the effect of biodegradation (Kerfoot 1987; Chan and Ford 1986). High clay content, organic matter, water content, and the processes of degradation can reduce the efficiency of

soil-gas sampling and therefore, cause contaminant concentrations to drop below detection limits.

The vadose zone is a highly complex soil-air-water-hydrocarbon system in which contaminants can move from one phase to another when affected by chemical, physical, and microbiological processes. In addition, the soil-gas sampling procedure itself causes disruption in the soil-gas equilibrium condition. As a result, subsequent soil-gas sampling very often produces different results and may not be comparable. Therefore, the data obtained can be compared only qualitatively.

Sampling Method

The selection of a soil-gas sampling method involves consideration of the type and the methodology of the sampling-system application, as well as the QA/QC protocol. There are approximately 100 soil-gas sampling systems in existence (Kerfoot and Sanford 1986; Eklund 1985; Mayer 1989; Spittler and Clifford 1985). According to ASTM Standard 5314-92, a soil-gas sampling method should be selected based on the consideration of the site-specific conditions. The six basic soil-gas sampling methods are listed below:

- (1) The whole-air-active method, which involves the sampling of a mixture of contaminant and noncontaminant vapors.
- (2) The sorbed-contaminants-active method of placing a sampling device in the subsurface and withdrawing soil gas through the device.
- (3) The whole-air-passive method of continuously injecting a carrier gas of a known composition and determining the contaminant concentration in a carrier gas-contaminant mixture.
- (4) The sorbed-contaminants-passive method of placing a collection device in the soil and allowing the device to equilibrate with the soil atmosphere.
- (5) Soil sampling and subsequent sampling of gas from a headspace atmosphere.
- (6) Soil-liquid sampling and subsequent sampling of gas from the headspace atmosphere of a liquid sample.

Whole-air-active methods of soil-gas collection involve the forced movement of soil gas from the soil to a collection device through a probe (Devitt *et al.* 1987; Kerfoot 1987). Contained samples of soil gas are then transported to a laboratory for analysis, or the sampling device is directly coupled with an analytical system. Whole-air-active sampling is best suited to soil-gas monitoring where contaminant concentrations are expected to be high and the vadose zone is vapor-permeable. Probes are installed into pre-existing holes or are driven into the vadose zone. The volume of a gas sample can vary from a few milliliters to several liters, depending on the sampling rate through the probe, the vapor storage capacity of the soil, and the soil's ability to deliver vapor to a probe under a vacuum.

The active approach may not be effective in clayey and moist soils. Driven probes tend to compact natural soils around the probe. In very dry soils, driven probes can create cracks that can enhance soil-vapor permeability and create pathways to the atmosphere. Under conditions of low soil permeability and low contaminant concentration, purging of the probe prior to sampling may lower contaminant levels below the limits of analytical detection. Discussions of numerous whole-air-active sampling systems can be found in Devitt *et al.* (1987), Boynton and Reuther (1938), and Nadeau *et al.* (1985).

Sorbed-contaminants-active methods involve forcing bulk soil gas from the soil to an apparatus designed specifically to extract and trap gas contaminants by adsorption. The adsorptive material used includes charcoal or a carbonized molecular sieve adsorbent (US EPA 1988b), porous polymers, silica gel, and activated alumina (Devitt *et al.* 1987). This system is well-suited to sites where the soil may be highly permeable to vapor and where the contaminant concentration may be lower than required for successful whole-air surveys. This approach is especially useful for the detection of nonpolar volatile organic compounds. Sorbent collection devices are commercially available or can be specially prepared with an appropriate sorbent material that concentrates desired compounds for future analysis. Colorimetric detector tubes are available that provide an indication of the presence of target compounds at the time of sampling.

These devices are limited in application by the high concentration requirements for many compounds and by the tube's compound-specific nature. The effectiveness of the sorbed-contaminants-active method is

limited in soils with high clay and water contents. Some sorbents may be affected by high humidity in soil gas. For example, for some chemicals, humidity greater than 60% (very common for soil gas) can reduce the adsorptive capacity of activated charcoal to 50%. The presence of condensed water in the sample tube may also indicate the reduced amount of adsorbed chemicals. Organic compounds that are reactive, oxygenated, or gaseous at room temperature are either not adsorbed by, or not efficiently desorbed from, charcoal tubes (US EPA 1988a).

Whole-air-passive methods involve continuously injecting a gas of known composition to create a small vacuum in a collection chamber, which results in the diffusion of soil-gas components from the soil into the chamber. The resultant carrier gas-contaminant mixture is collected for analysis. This method is effective in monitoring contaminant emissions from soil or water, and in assessing the health risk of such emissions to the general public. The air-passive method is limited in application because the injected gas greatly dilutes the contaminants in the sample stream. High water, clay, and organic matter content will restrict the rate of contaminant flux to the chamber.

Sorbed-contaminants-passive methods of soil-gas collection involve the passive movement of contaminants from the soil to a sorbent collection device. The main mechanisms of contaminant migration to a passive-sorbent device are (1) the diffusion of gas molecules from soil regions with a high concentration of gas to a sorbent device with a low concentration of gas, and (2) the advective transport of gas through the vadose zone intersecting the sorbent device. Passive samplers that have been used include occupational-health volatile-organic-compound monitors and a sampler originally developed to detect hydrocarbons in petroleum exploration (Spittler and Clifford 1985; Wesson and Armstrong 1975). These devices use containers that are several inches in diameter and that utilize charcoal as a sorbent. The end of the instrument is left open and the device is placed in a borehole at the desired depth. The borehole is then backfilled (Mayer 1989), and the sorbent device is usually left in the soil for two to ten days, or in some cases, up to 30 days or more. This method can be used even in frozen and high-water-saturation soils (Wesson and Armstrong 1975).

Soil sampling for subsequent headspace atmosphere or extraction sampling methods are used to determine contaminants present in a headspace atmosphere above a contained soil sample. Note that this head-

space atmosphere is not gas extracted from the soil, rather it is an artificial atmosphere that volatilized from a potential contaminant source, that is, the soil sample. Contained atmosphere methods do not yield representative samples for *in situ* vadose zone investigations, because the sampled soil gas is not the same gas as the *in situ* vadose zone gas. During sampling, large amounts of the vapor phase can be lost, which reduces the applicability of this method. Uncontrolled volatilization can be reduced using two methods: (1) recovering small soil cores with polypropylene syringes, or (2) adding buffering solutions or sodium sulphate and phosphoric acid to the vial prior to sealing, which will shift the activity coefficients of the subject contaminants to favor the vapor phase. To reduce contaminant degradation (especially biodegradation) in the container, samples should be stored in the dark at approximately 4°C.

Soil pore-liquid headspace gas methods involve the collection of soil gas that has accumulated above the soil pore liquid in suction lysimeters, pan lysimeters, or free-drainage glass block samplers. After a lysimeter has been installed for some period of time, vapor is sampled from a soil pore liquid sampler. In dry soils, when the lysimeter cannot recover a pore liquid sample, the soil gas can freely pass through the porous cup of the lysimeter, and the suction lysimeter serves as a soil gas sampler. Soil-gas samplers can be installed at different depths in vertical or slanted boreholes. The space between the samplers should be properly backfilled in order to avoid cross-contamination.

Soil-gas sampling should involve the collection of field blanks, travel blanks, and sample probe blanks to test for residual contamination in the sampling system, and to examine sample integrity during handling and transport. Field replicates can be demanded by a client or dictated by a particular situation. The number of replicates is usually 10% of the total number of soil-gas samples. In general, the time between sample collection and analysis should be minimized. Investigators should also protect samples against light and heat, and exercise precautions against leaks (see ASTM Practice D 1605).

Problems of sample handling and transport can be minimized by the integration of sampling and analytical systems. For example, a whole-air-active-sampling system can be coupled directly to a portable VOC (volatile organic compound) analyzer. The sample stream is fed directly to the intake port of the analyzer and passed through the detector.

Small volume samples are commonly recovered by syringe for immediate injection into an analyzer or small-volume container. Glass gas-tight chromatography syringes are employed when rigorous QA/QC protocol is required and samples are injected into the analyzer immediately upon recovery. These syringes must be decontaminated prior to the recovery of each sample aliquot. Disposable syringes are employed when samples are to be transferred to a small-volume container for transport.

Hand pumps are also used to transfer samples into tedlar bags or glass bulbs. Hand pumps are preferably installed behind the analyzer or container in the sample train to avoid contribution from or loss of contaminants to the hand pump. Hand pumps commonly contain petroleum-based lubricants, which will contribute to the hydrocarbon content of soil gas. These devices must be either placed at the end of the sample train or abandoned.

For low-level detection, tubing can cause a cross-contamination if it is not replaced in the sampling train prior to sampling at a new location. Vacuums can be employed to transfer soil gas from a sampler to a container. Evacuated glass bulbs, some containing adsorbents or absorbing liquids (see ASTM Practice D 1605), can be affixed to an in-place, purged sampling device and allowed to come to pressure equilibrium. Care must be exercised in recovering the gas sample from a vacuum cylinder to avoid contaminating the sample with atmospheric air.

Sorbent traps are commonly self-contained. A trapping device should be compatible with the properties of the target compounds and the technique of desorption chosen. Good practice for use of these devices, including handling and desorption procedure, is required for successful implementation of sorbent traps when sampling organic compound vapors (see ASTM Practice D 3686). Containers for soil samples should be preserved for a subsequent headspace analysis. The choice of container for soil headspace determination is dependent upon the method of sampling chosen.

Soil-gas samples have limited holding time depending on the degradation of the VOCs in the container, which may be caused by exposure to light or heat, agitation during shipping, as well as the air diffusivity of the container material. Sample biodegradation may occur in containers if the water vapor condensed in a container contains microorganisms capable of metabolizing contaminants.

On-Site Measurements

Flame Ionization Detectors (FIDs) generate electric current when gases containing carbon atoms are oxidized to carbon dioxide in a hydrogen flame and potential is applied across the flame. The magnitude of the electric current generated is termed the detector response. FIDs are responsive to hydrocarbon contaminants in soil gas and are therefore commonly employed as contaminant detectors. These detectors are durable for field application, have a wide linear range, and generally respond uniformly to organic gas species. FIDs are usually unresponsive to inorganic gases and water vapor, which are common constituents in soil gas. FID performance can be evaluated independent of the chromatographic column (see ASTM Practice E 594). Although highly versatile, these detectors are not selective for halogenated compounds. They require supplies of fuel gas, which necessitate careful safety practices in handling and flame ignition.

Photoionization Detectors (PIDs) employ ultraviolet radiation to ionize organic molecules. Positive ions and free electrons are formed, which migrate to the detector electrode(s), resulting in an electric current that is proportional to the contaminant concentration at the detector. PIDs are extremely sensitive to aromatic hydrocarbons. The range of detectable contaminants can be extended by using lamps of different energies, which will cause a change in the response of contaminants with different ionization potentials.

Figure 3-32 summarizes the data illustrating the relationship between PID readings taken in the field and the total VOC concentrations determined using sampling of soil gas into 1L SUMMA canisters and the TO-14 EPA analysis of soil gas. Data from all available soil gas probes within LBNL are included in the figure. A nearly 1 to 1 linear relationship between the PID reading and the total VOC concentration can be used to describe the data at VOC concentrations that exceed 1000 ppbv. However, when the actual VOC concentrations were lower than 1000 ppbv, the PID equipment could not accurately measure the concentration. In this case, the PID either registered a null sample (Group 1) or over-predicted the actual concentration (Group 2).

Electron Capture Detectors (ECDs) are highly sensitive to and selective for compounds with electronegative functional groups such as chloro-fluorocarbons (CFCs). The sensitivity of the detector is propor-

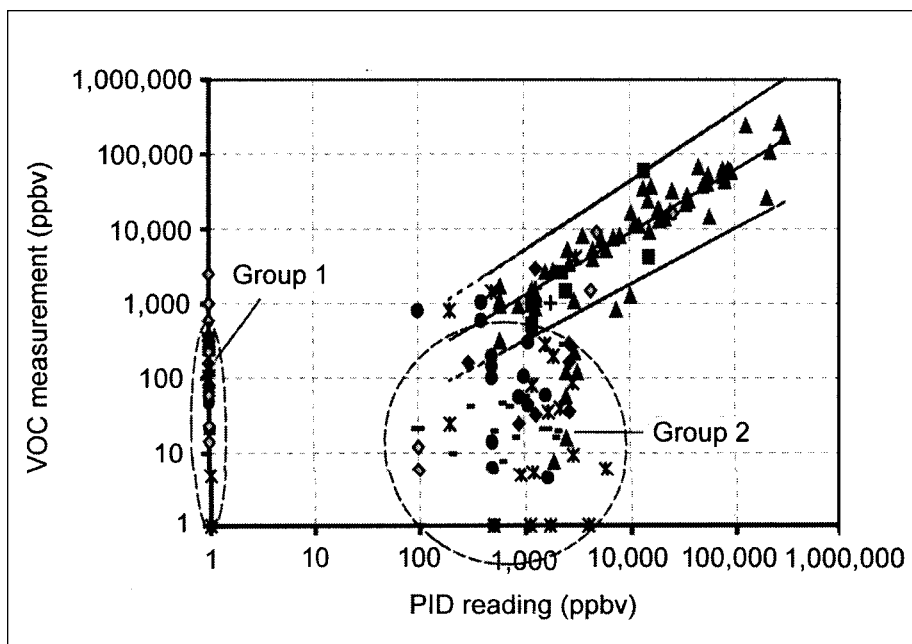


Figure 3-32. Relationship between PID and VOC measurements taken at all available gas probes at LBNL

tional to the number of these groups on a compound, resulting in a detector response that is unique to each compound. The ECD comprises a source of thermal electrons inside a reaction chamber (a radioactive source emits β radiation, which ionizes the carrier gas to produce electrons). The device detects compounds with electronegative functional groups capable of reacting with thermal electrons to form negative ions. Such reactions decrease the concentration of free electrons, and the detector is designed to measure such changes in electron concentration inside the chamber (see ASTM Practice E 697). Calibration of the ECD is therefore linked to each compound and is determined by the detector. ECDs are also sensitive to water, oxygen, and other common components of soil gas, which may cause problems in method performance. Because ECDs emit radiation, the space should be properly vented, and under Federal regulation, licensing is required for ECD operation.

Other detectors that provide soil-gas analysis are the argon ionization detector (a nondestructive device similar in operating design to the ECD), the flame photometric detector (FPD) used to determine organic compounds containing sulfur and phosphorus, and the hot-wire (pyrolyzer) detector used to identify compounds containing nitrogen.

The selection of a particular soil-gas monitoring technique should always be based upon the physical properties of the vadose zone, the chemical and physical properties of the compounds of interest, and the type of the remediation system. A case study on the accompanying CD shows three applications of an innovative *in situ*, real-time automated soil-gas detection and monitoring system, MultiScanTM. The uses of the Multi Scan System demonstrated in this case study “MultiScanTM Case Study #1: Los Alamos National Laboratory Vapor Extraction System, and MultiScanTM – Case Study #2: Subsurface Barrier Verification,” are listed below:

- (1) Monitoring and performance assessment of the Pilot Vapor Extraction Test was conducted at Los Alamos National Laboratory. The soil gas probes were embedded in monitoring boreholes using the SEAMISTTM system. A photoacoustic gas analyzer was used to detect TCA, TCE, Freon, CCl_4 , CO_2 , and water vapor. Barometric pressure and temperature were measured.
- (2) Subsurface barrier verification was used in combination with the SEAttraceTM to locate leaks in a colloidal silica permeation-grouted barrier at Brookhaven National Laboratory and a thin-wall jet-grouted barrier at the Dover Air Force Base.
- (3) Monitoring and performance assessment of a passive vadose zone remediation system (BERTTM) was completed at the Radioactive Waste Management Complex of the Idaho National Engineering and Environmental Laboratory.

Soil-Gas Sampling for Radon*

Radon is a radioactive gas that is generated naturally by the radioactive decay of radium, an element that is contained in all rocks and soils.

*This section was contributed by A.R. Hutter and B. Faybishenko.

Recent investigations have found that radon (^{222}Rn) concentrations measured in soil gas and groundwater can be used to detect tectonic structure and the weak zones in the near-surface zones (Choubey and Ramola 1997). Hutter (1996) identified the factors affecting radon migration in soils, which are humidity, porosity, barometric pressure, wind, precipitation, temperature, and soil permeability. Each parameter strongly correlates with the radon concentration. The factors controlling the spatial and seasonal variations in radon concentration are the local soil conditions, moisture content, and temperature (Rose *et al.* 1990; Hutter 1996). Radon migration along deep cracks to the surface can be caused by a combination of several processes such as diffusion, barometric pumping, and thermal convection (Rose *et al.* 1990).

The isotope ^{220}Rn is known as thoron. It has a half-life of approximately 55 seconds. Hutter (1995) showed that the ratio of ^{220}Rn to ^{222}Rn can be used to assess the soil-gas processes. A case study on the accompanying CD, "Investigation of Fast Migration in the Vadose Zone for Assessment of Groundwater Contamination by Chernobyl Radionuclides," by V.M. Shestopalov, V.N. Bubilas, and D.U. Kukharensko, Radioecological Center, NAS of Ukraine (based on the results of investigations in the Chernobyl area vadose zone) demonstrates that the increased ratio of ^{220}Rn to ^{222}Rn indicates a zone of potential preferential flow in the vadose zone. Isotopic studies were confirmed using radar measurements.

The methods used for soil-gas sampling typically involve emplacing tubes into the ground permanently or temporarily, depending upon the requirements of the sampling program. Generally, permanently emplaced tubes help to ensure more accurate analytical results because of possible changes of the soil structure around the tubes during installation. Soil gas is then extracted from these tubes and analyzed for the radon isotopes ^{220}Rn and ^{222}Rn , using scintillation cells and gross alpha counting equipment or solid-state alpha spectroscopy instruments. For instance, a typical soil-gas-sampling set-up is shown in the DOE *Environmental Measurements Laboratory's Procedures Manual* (EML 1997).

Methods of determining ^{220}Rn and ^{222}Rn contamination using with soil-gas samples have been widely published (Hutter 1995; Lahti *et al.* 1998). Using these methods to measure typical soil gas ^{220}Rn and ^{222}Rn concentrations (greater than 5 kBq m^{-3} [130 pCi L^{-1}]), Hutter (1995)

showed an uncertainty of 20.7 percent and 10 percent (90 percent confidence levels), respectively, from analyses of duplicate field measurements.

An international comparative study of soil-gas radon measurements was conducted in 1995. The results, based on pooling of the participant data and use of the ratio of the standard deviation (SD) to the arithmetic mean, showed an agreement of approximately 27 percent at depths greater than 0.75 m (Hutter 1998). From this study, it was concluded that sampling errors are two to three times that of analytical errors.

Many factors may introduce significant errors during soil-gas sampling. For instance, if a loosely fitting sample tube is inserted into a drilled hole with only a plug at the surface, the soil gas that is drawn is probably not from the depth of the tube bottom, but rather, from some unknown and varying depth along the length of the tube. Using “packers,” or very small diameter probes, helps to ensure proper depth determination (Tanner 1988; Reimer 1990). Inherent in this consideration is the “target” volume of the sampled soil gas. Even though sampling depths may be similar, the measured ^{222}Rn concentration may be influenced by the volume of the sample, as a result of vertical variation in the soil gas ^{222}Rn concentration. Samplers that draw a large volume of soil gas are likely to introduce a greater uncertainty because of vertical variation in soil-gas radon. For example, a 1 L soil-gas sample drawn from the bottom of a tube is likely to come from several centimeters above and below the tube end (assuming packers are not used). On the other hand, small sample volumes of extracted soil gas are more likely to have been derived from a smaller zone. The data from the comparative study described above indicate that, for the test site, a greater error was introduced by poor estimation of the soil-gas extraction depth than by any variations in ^{222}Rn concentrations caused by soil heterogeneities (Hutter 1998).

Pneumatic Pumping and Injection Experiments

Pneumatic pumping and injection experiments using boreholes screened in the vadose zone are important for many environmental and engineering applications including soil vapor extraction (SVE) systems. SVE systems are widely used for remediation of volatile and semi-volatile organic compounds accumulated in the vadose zone from leak-

ing surface and underground tanks, pipelines, cribs, spills, and other sources, at many contaminated sites (Massmann 1989; Pedersen and Curtis 1991). The design of soil vapor extraction systems is based upon the results of pneumatic (gas) pumping and/or injection experiments conducted to determine the soil air permeability and porosity, which are then used in assessing the well spacing, well configuration, and blower or pump specifications (Pedersen and Curtis 1991; Massmann and Madden 1994). Pneumatic injection and pumping experiments can be conducted independently or simultaneously using different wells.

Single-and cross-borehole air-injection interference tests can be used to characterize unsaturated heterogeneous soils and fracture networks. To conduct the field tests in fractured rocks, strings of straddle packers fitted with injection and monitoring ports are employed to seal off discrete depth intervals in different boreholes (Cook 1999). Field experiments in unconsolidated sediments are typically conducted by connecting a blower up to the top of the well casing and injecting or extracting air from the well screened interval. Figure 3-20 shows a schematic of the automatic packer design. Ambient-temperature air or a gas-tracer can be injected at a constant mass rate into a given depth interval in an injection well, and pressure responses are measured at different intervals in monitoring wells. The first type of test represents zero-offset profiles (ZOP), in which the injection packer string and monitoring strings are moved together along the length of the borehole by the same increment. The second type of test represents multiple-offset profiles (MOP), with monitoring locations in other wells, which are held fixed while the injection zone is moved incrementally along the length of the borehole. These tests can be repeated systematically for different combinations of wells, and injection and monitoring intervals. The changes in the injection mass flow and pressure response are used to assess the three-dimensional pneumatic connectedness of the formation (Benito *et al.* 1999; Cook 1999). This type of information can be combined with geophysical, geologic, and other hydrologic data to improve the understanding of flow paths and develop an adequate conceptual model of the site.

Air-injection tests have been successfully used in determining the air permeability and the geometry of flow in relatively dry soils and fractured rocks at several sites (Rasmussen *et al.* 1995; Granovsky and McCoy 1997; Illman *et al.* 1998; Benito *et al.* 1999). For example,

air-injection tests have been used successfully at the Yucca Mountain Site in Nevada, which is a potential site for a geologic high-level nuclear waste repository. To date, an estimated 3,500 separate air injections have been undertaken, and nearly a quarter of a million pressure-response curves have been logged in the study (Cook 1999).

Pneumatic pumping experiments are conducted by extracting gas from a borehole at an open (or screened) interval and measuring spatial and temporal distributions of the decrease in the gas pressure using pressure sensors installed in the injection and observation wells. For example, Figure 3-33 shows schematics of the vacuum extraction from a soil profile open to the atmosphere. The flow pattern developed around the

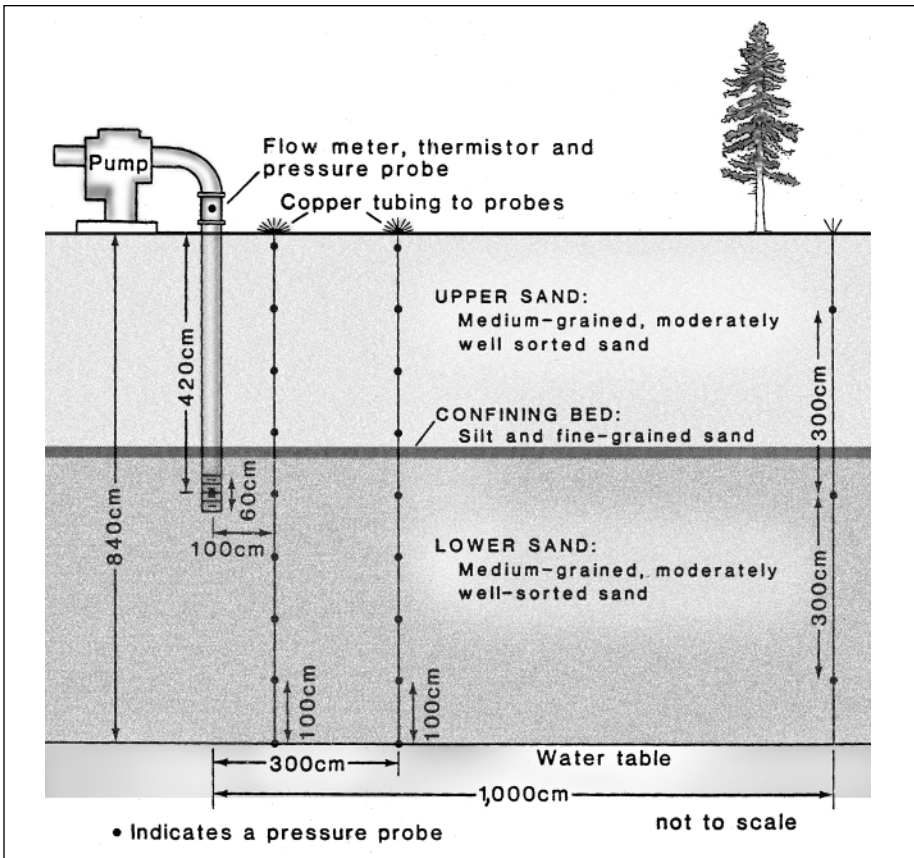


Figure 3-33. Schematic of site instrumentation for conducting pneumatic tests in the vadose zone (Baehr and Hult 1989).

injection well depends on the boundary conditions. The design and performance of the pneumatic pumping tests are described in detail by, Cho and DiGiulio (1992), Edwards and Jones (1994), Massmann (1989), and Massmann and Madden (1994).

Models of Airflow

Contrary to liquid flow in porous media, the gas velocity at the pore wall cannot always be assumed to be zero. This is because of an additional flow component termed the “slip flow” or “drift flow” (Klinkenberg 1941), also known as “Klinkenberg’s effect.” Klinkenberg’s effect leads to the total gas flow exceeding the viscous flow predicted by Darcy’s law. The ratio of the slip flow to the viscous flow increases as the average pore radius decreases. For example, the effect of slip flow is important in silt and clay sediments when the pore radius is less than approximately 10^{-3} mm. The effect of slip flow is negligible in sand and gravel materials when the pore radius is from 10^{-2} to 10^{-1} mm and larger (Massmann 1989).

Assuming the validity of Darcy’s law for flow of ideal gas of a constant viscosity and composition in isothermal and constant volumetric gas content media, and neglecting slip flow, transient gas flow is described by a nonlinear equation (Bear 1972):

$$nS_g\mu \frac{\partial P}{\partial t} = \nabla(\mathbf{k}_g P \nabla P) \quad (3.4)$$

where n = porosity, S_g = gas saturation, μ = gas viscosity, P = gas pressure, and \mathbf{k}_g = gas-permeability tensor (including gas phase relative permeability effects). This nonlinear equation can also be written in terms of the pressure squared:

$$\frac{nS_g\mu}{P} \frac{\partial P^2}{\partial t} = \nabla \mathbf{k}_g \nabla P^2 \quad (3.5)$$

Table 3-14 summarizes the assumptions and corresponding limitations used in deriving a model of gas flow in porous media described by equations (3.4 and 3.5). For small pressure gradients, a linear approximation of equation (3.4) can be used (Massmann 1989)

TABLE 3-14 Summary of Assumptions and Limitations (After Massmann 1989)

Assumptions	Limitations
The equation of motion for gas transport can be approximated using equations similar to Darcy's law	In fine-grained materials, Darcy's law underestimates discharge by neglecting slip flow; however, this assumption is likely a valid approximation for flow in sand and gravel
Effects of diffusional flow are negligible	Valid assumption for predicting pressure distributions
Vapor behaves as ideal gas	Valid approximation of temperature and pressure conditions typical for vapor-extraction systems
Constant and uniform porosity	Porosity will generally vary with time and with location due to natural variations in geologic materials and temporal and spatial variations in moisture content
Molecular weight is uniform	Molecular weight will vary with gas composition; variations will generally be small for typical applications of methane control and organic vapor recovery
Gravitational effects are negligible	Valid assumption for vapor extraction applications
Compressibility of the porous media is negligible	Valid assumption because compressibility is essentially small as compared to that of vapor
Gas transport can be modeled using the equation for incompressible flow	Valid assumption for pressure variations on order of one-half an atmosphere and less

$$nS_g \mu \frac{\partial P}{\partial t} = \nabla(\mathbf{k}_g P_o \nabla P) \quad (3.6)$$

where P_o = initial or static gas pressure. For larger pressure gradients, it is more accurate to linearize equation (3.5):

$$\frac{nS_g \mu}{P_o} \frac{\partial P^2}{\partial t} = \nabla \mathbf{k}_g \nabla P^2 \quad (3.7)$$

Equations (3.6 and 3.7) show that five parameters are needed to simulate gas flow, including viscosity, average gas pressure, porosity, gas saturation, and the gas phase permeability (the product of the intrinsic permeability and the gas phase relative permeability) of the porous media. Note that equations (3.6 and 3.7) assume a constant volumetric gas content (the product of gas-phase saturation and the porosity) and a constant gas composition. It should be noted here that while analytical gas flow models are usually based on equations (3.6) or (3.7), several numerical simulators are capable of solving the more general problem with mixtures of nonideal gases, slip flow and variable gas saturation (see Chapter 5).

Analytical and Numerical Solutions and their Limitations

Analytical solutions of equation (3.7) for air permeability are usually based on assumptions of either one-dimensional radial (McWhorter 1990) or two-dimensional radial and vertical axisymmetric flow of compressible air toward a partially penetrating well screened in the vadose zone (Baehr and Hult 1989, 1991; Massmann 1989; Shan *et al.* 1992). Falta (1996) developed a program called GASSOLVE for analyzing several types of transient and steady-state soil gas pump tests, which are listed in Table 3-15. In developing his program, Falta (1996) used analytical solutions from Hantush (1964), Baehr and Hult (1989), and Falta (1993).

Illman *et al.* (1998) analyzed the data of a series of multistep, single-hole pneumatic tests conducted by Guzman *et al.* (1994) and Guzman and Neuman (1996) that used transient pressure and pressure-derivative type-curve methods. They determined that airflow around the 1-m long borehole injection intervals appeared mostly to be three-dimensional; air compressibility led to a significant borehole storage effect, rendering the first step of a single-hole test to be unreliable; borehole skin effects were minimal; and air permeabilities determined from steady-state and transient-type-curve methods were practically the same. The accuracy of estimates of air-filled porosity and air permeability increases if multistep injection experiments are complemented by air-pressure recovery experiments (Vesselinov and Neuman 1999). However, an application of the type-curve approach is limited because the subsurface formation around the injection interval is assumed to be homogeneous, a linear equation of airflow is used, and the borehole storage effect is taken into

TABLE 3-15 Types of Gas Pump Tests Analyzed by GASSOLVE (Falta 1996)

Type of soil gas pump test	Parameters to be determined
Transient, open to the atmosphere	$k_r, k_z, (\theta_g)$
Steady-state, open to the atmosphere	k_r, k_z
Transient, fully confined, fully penetrating well	$k_r, (\theta_g)$
Transient, fully confined, partially penetrating well	$k_r, k_z, (\theta_g)$
Transient, leaky confining layer, fully penetrating well	$k_r, (k'/h'), (\theta_g)$
Transient, leaky confining layer, partially penetrating well	$k_r, k_z, (k'/h'), (\theta_g)$
Steady-state, leaky confining layer, fully penetrating well	$k_r, (k'/h')$
Steady-state, leaky confining layer, partially penetrating well	$k_r, k_z, (k'/h')$

Legend: k_r = radial air permeability,
 k_z = vertical air permeability,
 k' = permeability of the leaky confining layer,
 h' = thickness of the leaky confining layer.

account only for a single monitoring interval at a time, neglecting the air storage effect in the rest of the injection borehole.

Numerical inverse modeling has several advantages over analytical methods. For example, Vesselinov and Neuman (1999) considered air-flow through a nonuniform, locally isotropic, porous continuum system, including all boreholes with multiple packed-off intervals, and simultaneously measured pressure data at several monitoring intervals, taking into account atmospheric pressure fluctuations. Their method also provided kriged estimates of spatial variations in air permeability and air-filled porosity throughout the tested fractured rock volume.

Analytical and numerical solutions of airflow equations often assume constant parameters; however, parameters may vary with time because of a variety of processes affecting airflow. If one neglects these processes, one may obtain erroneous prediction results and then design ineffective remediation systems. For example, gas flow in the subsurface can induce volatilization and evaporation of liquid water and nonaqueous phase liquids (NAPLs). These changes in the liquid saturation can

have a significant effect on the gas phase relative permeability. Vacuum pumping involves both radial air movement from the soils surrounding the well and vertical flow from the atmosphere through an uncovered land surface or cracks in the cover (Edwards and Jones 1994). Neglecting the leakage through a soil cover (for example, through cracks in asphalt) toward the pumping well is a source of errors in the determination of air permeability (Massmann and Madden 1994).

The values of air permeabilities determined from field tests may be several orders of magnitude higher than those determined from laboratory core experiments and the permeability determined from hydraulic tests (Guzman *et al.* 1996). This is mainly because air permeability determined using laboratory cores represent the rock matrix and air permeability determined using field experiments represent a soil/rock system affected by zones of fast, preferential flow. Such zones are usually absent in small laboratory cores. However, the complexity of the flow field in a heterogeneous formation leads to a poor correlation between the values of air permeability and the fracture geometry parameters—such as density, trace length, orientation, aperture, and roughness (Neuman 1987). Because the directions of airflow depend on a combined effect of the geometry of the injection interval, flow paths in the fractured-porous system, and boundary conditions, the flow dimensionality may not be an integer (1, 2, or 3). It can be a noninteger or fractional (Barker 1988).

Massmann and Madden (1994) demonstrated that the air conductivity determined using horizontal wells was about twice that determined using vertical wells. Cho and DiGiulio (1992) demonstrated that horizontal permeabilities determined from air-injection tests are slightly higher than those determined from vacuum extraction tests. The difference can be caused by subtle layering or soil stratification at the sites. Because the range of air permeability determined from small-scale core measurements and single-hole experiments varies randomly in space by orders of magnitude and exceeds the range of air permeability from the variations of applied pressure, one can use geostatistical methods to analyze the spatial distribution of flow parameters.

Air permeability determined from air-extraction tests can be as much as 20% larger than that from injection tests (Massmann and Madden 1994). The reason for this is that the injection of warmer air in the formation (which usually has a lower temperature) results in water con-

densation in the near-well zone. To avoid this problem, it is recommended to use N_2 gas or run the ambient air through a desiccant before injecting it into the well.

Because air permeability is a function of the soil moisture content, an increase in the moisture content of soils leads to a reduction in air permeability (Stonestrom and Rubin 1989a, b; Guzman *et al.* 1994; Guzman and Neuman 1996). Because the matrix water saturation is usually higher than that of fractures, the matrix air permeability may become insignificant compared to that of unsaturated, air-filled fractures. In this case, the air permeability can be determined using numerical inverse modeling by treating air as a single mobile fluid phase in a continuum medium represented primarily by interconnected air-filled fractures (Vesselinov and Neuman 1999).

Air injection into a formation containing some moisture causes pressure buildup followed by a slight drop, as water is pushed away from the near-borehole zone or it evaporates. The amount of time required for pressure in the injection interval to stabilize typically ranges from 30 to 60 minutes. However, as the flow rate increases, the nonsteady flow regime may last for 24 hours or longer, as a result of water displacement from air-conducting fractures. Consequently, the gas permeability increases. Thus, short-term air-injection tests may lead to an incorrect estimation of air permeability. In large open fractures (or fracture zones), the inertial effects grow as the applied pressure increases. Experimental observations in fractured rocks have shown that the relationship between air-pressure change and the airflow rate, which takes into account both viscous flow and inertia effects, is given by (van Golf-Racht 1982)

$$\Delta(P^2) = AQ + BQ^2 \quad (3.8)$$

where A and B are coefficients representing the effects of viscous (laminar) and inertial (turbulent) flow, respectively. The values of A and B can then be used to calculate the rock permeability (van Golf-Racht 1982). Equation (3.3.11.4-5) can be represented as

$$Q/\Delta(P^2) = 1/(A + BQ) \quad (3.9)$$

where the ratio $Q/\Delta(P^2)$ is called the gas deliverability index (van Golf-Racht 1982), which characterizes the ability of soils/rocks to transmit gas.

An alternative to pneumatic pumping and injection experiments is the determination of the vertical air permeability of the unsaturated soils and rocks using the analysis of the time trend of atmospheric pressure and air pressure at different depths of the vadose-zone profile (Weeks 1978; Shan 1995).

Thus, because a variety of environmental processes and factors affect air pumping/injection and the test design, one needs to study airflow processes and determine air permeability by taking into account site-specific conditions and using the same well design as planned for the SVE system (Cho and DiGiulio 1992). It is important to conduct air-injection experiments using single-hole or cross-hole air-injection tests at several applied flow rates and pressures.

MONITORING FOR NONAQUEOUS PHASE LIQUIDS*

The removal of residual solvents, primarily dense nonaqueous-phase liquids (DNAPL), is currently the most significant challenge for the successful completion of many large groundwater and soil-cleanup efforts. Slowly dissolving DNAPL may provide a major source of vadose zone and groundwater contamination for hundreds of years. The problem is further complicated by the fact that DNAPLs are present as dispersed blobs at many sites and are therefore very difficult to characterize in the subsurface. At waste sites where DNAPL contamination is suspected, robust characterization of the nature and extent of the contamination is an essential component of any comprehensive remediation strategy.

Traditional sampling approaches usually are unsuccessful in locating DNAPL. Many of the current methods used for characterizing DNAPL-contaminated sites are described by Cohen and Mercer (1993). These methods generally consist of inferred measurements of DNAPL (such as soil-gas analysis and geophysical methods), rule-of-thumb empirically developed methods from aqueous well samples, and direct measurements using invasive methods such as drilling and soil sampling. Most

*This section was contributed by Joe Rossabi, Carol Eddy-Dilek, and Brian Riha.

geophysical techniques do not have the resolution needed to detect DNAPL present at scales smaller than one cubic meter. Conventional soil and liquid sampling are too costly to be used for detailed DNAPL characterization. However, precise delineation of DNAPL-contaminated areas will facilitate the design of appropriate remediation strategies and prevent the escalation of cleanup costs.

Because of the complexity of spatial distribution of DNAPL in the subsurface, several characterization methods should be used in an ensemble approach. The techniques described in this section were designed specifically for implementation with the cone penetrometer (CPT). This takes advantage of the high-resolution geologic information obtained with the CPT.

Above the water table, DNAPL resides in intergranular pores held by capillary forces. Below the water table, DNAPL behaves in a complex fashion, moving downward as an immiscible phase and accumulating in highly concentrated discrete and dispersed ganglia. Because of the physical and chemical characteristics of DNAPL, characterization and remediation methods that minimize unnecessary waste generation are prudent.

Many strategies and tools target the refractory case of DNAPL occurring in thin, highly discrete zones, which are typical of most sites. The innovative DNAPL characterization tools that have proved to be most successful in field tests include: (1) hydrophobic sorbent ribbon on FLUTe™ (also known as SEAMIST™) membrane, and (2) Laser-Induced Fluorescence (LIF), Raman, and Optical Cone Penetrometer Test (CPT) probes. The case study “Cone Penetrometer-Based Raman Spectroscopy for DNAPL Characterization in the Vadose Zone,” by J. Rossabi, B.D. Riha, J. Haas, C.A. Eddy-Dilek, A. Lustig, M. Carrabba, K. Hyde, and J. Belo, provides a detailed description of the cone penetrometer-based Raman spectroscopy.

These technologies have been successfully demonstrated and will complement tools currently used or proposed by industry, DOE, the U.S. Environmental Protection Agency (EPA), and the U.S. Department of Defense (DoD). The innovative characterization technologies (such as CPT-based Raman and FLUTe™) build on the baseline DNAPL characterization techniques and generally strive for direct detection of DNAPL with minimal invasion and minimal investigation-derived waste (IDW).

In addition, several other promising technologies have been tested, such as alcohol micro-injection/extraction through CPT, differential-partitioning gas tracer tests, and measurement of radon partitioning to DNAPL. However, these technologies require additional development.

At the DOE Savannah River Site, a package of innovative DNAPL characterization tools is being developed and deployed to:

- Unambiguously identify DNAPL in the subsurface
- Minimize secondary waste
- Eliminate undesirable gravitational movement of DNAPL
- Minimize IDW
- Mitigate similar types of collateral environmental damage inherent in addressing this complex environmental need.

Rapid Hydrophobic Sampling

The rapid hydrophobic sampling system is fast and easy to deploy with a cone penetrometer system, and it yields depth-discrete samples from boreholes. For this technique, hydrophobic sorbent ribbons (that is, ribbons that preferentially absorb non-polar liquids) are attached to the liner of small-diameter FLUTE membranes (see the subsection “Removable SEAMIST™ Liners,” above). The ribbons are designed to collect DNAPL samples (Figure 3-34), and are impregnated with a DNAPL indicator dye for immediate assessment of the presence of DNAPL’s at a specific depth. The ribbon is pressed against the formation on the walls of the borehole, and the hydrophobic material preferentially collects organic liquids. The liner is then retrieved from the borehole and is rapidly scanned both visually and with a volatile organic compound (VOC) analyzer. After screening, the depth-discrete sorbent pads can be analyzed in more detail in the laboratory. The FLUTE can also be deployed using drilling methods.

Laser-Induced Fluorescence (LIF), Optical, and Raman-Cone Penetrometer Methods

The cone penetrometer is particularly suited for characterization of DNAPL-contaminated sites because of its ability to deploy a variety of



Figure 3-34. Picture of FLUTE™ membrane recovered from a CPT borehole. Dark marks indicate DNAPL at that depth.

sensors as well as its capacity to delineate depth-discrete lithology and contaminant distribution with relative ease. Because chlorinated alkanes do not fluoresce at standard excitation wavelengths, LIF sensors cannot measure chlorinated alkanes directly. However, fluorescent intensities are found to increase one to three orders of magnitude over the background in zones known to contain DNAPL. The large increase may be due to the leaching of natural organic matter or the incorporation of other likely fluorophores into the DNAPL. Co-disposed lubricants, hydraulic oils, and cutting oils are also potential candidates for fluorescence probing. Thus, the fluorescence measurements can be used to infer the presence of DNAPL. Used in concert with Raman spectra, the presence of DNAPL in a particular location can be confirmed. For details of this method, see the case study “Cone Penetrometer-Based Raman Spectroscopy for DNAPL Characterization in the Vadose Zone, by J. Rossabi, B.D. Riha, J. Haas, C.A. Eddy-Dilek, A. Lustig, M. Carrabba, K. Hyde, and J. Belo.”

Raman spectroscopy is one of the few direct detection-characterization technologies for DNAPL. Each compound has a unique Raman spectrum that can be probed through the optics deployed in a cone penetrometer. Thus, specific DNAPL compounds can be identified. Unfortunately, the Raman technique is inherently weak, and the spectra must be separated from the fluorescence spectrum, which often dominates over it. Other optical techniques such as CPT video microscopy (for example, the Navy GeoVis system) have also helped to identify DNAPL in the subsurface. Specific formations can be visually identified for DNAPL potential for precise targeting by spectroscopy. If co-constituents color the DNAPL, DNAPL may be directly identified.

Small-Scale Alcohol Micro Injection/Extraction Test

The single-well, alcohol injection-extraction test uses a cone penetrometer delivery system through which less than one gallon of a solution of alcohol is injected. The injected fluid permeates into an area of the size of a small cylinder around the CPT, and can solubilize DNAPL without mobilizing it. A small volume of water is injected a small distance into the formation (less than 1 ft) and is then extracted. The extracted water samples are analyzed to determine the concentration of organic contaminants. Then, a small volume of an alcohol and water solution is injected a similar distance into the formation and is subsequently extracted. The extracted solution is sampled and analyzed. DNAPL is significantly more soluble in the alcohol/water solution than in water alone. A large increase in the concentration of DNAPL components is an unequivocal indicator of the presence of residual DNAPL. The test provides clear confirmation of the presence of DNAPL without the drilling of additional holes. The test has been used to target specific strata that were thought to contain DNAPL (that is, above clay in the saturated zone).

Limitations

The use of CPT technologies is limited to unconsolidated sediments and to depth refusal of the cone penetrometer. Comparison of the results of the DNAPL detection using core sampling, Raman spectroscopy, and FLUTE data shows that the data complement each other. However, we

cannot obtain a unique result about the DNAPL distribution from single-borehole measurements (Figure 3-35). At the same time, the design of remediation requires knowledge of the total volume of DNAPL in the subsurface. For this purpose, cross-borehole, partitioning interwell tracer tests can be used.

The case study “The First Vadose Zone Partitioning Interwell Tracer Test (PITT) for NAPL and Water Residual,” by Paul E. Mariner, Minquan Jin, James E. Studer, and Gary A. Pope, describes a method of estimating the total volume of DNAPL in subsurface. See page 491.

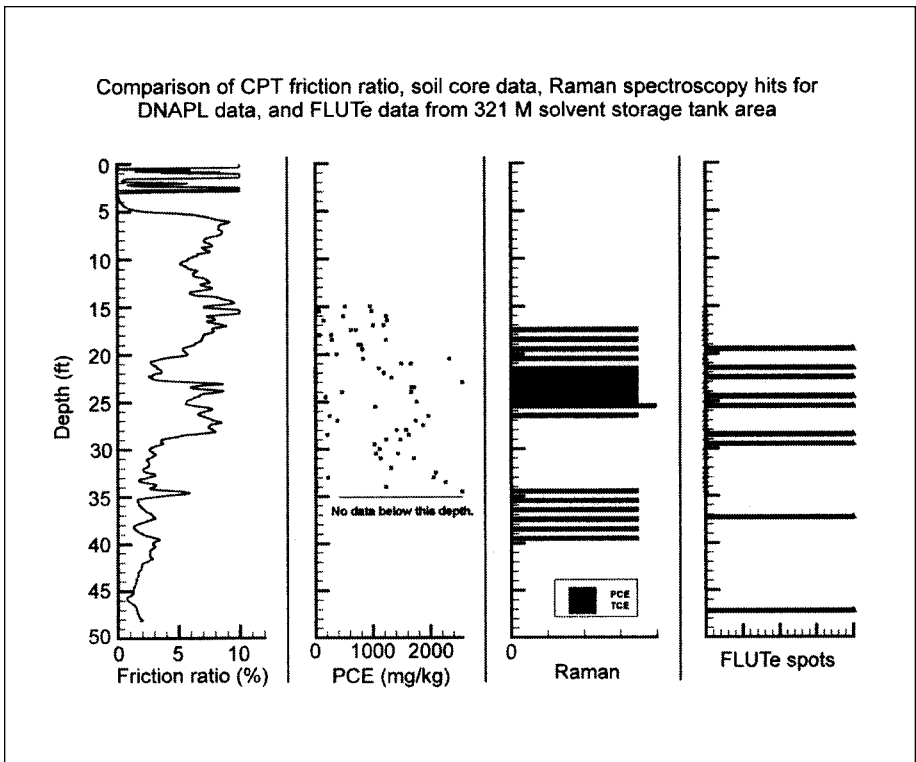


Figure 3-35. Plots indicating CPT lithology, sediment sampling and analysis, CPT Raman spectroscopy identification of PCE and TCE, and FLUTE membrane identification of DNAPL contamination at SRS solvent storage tank area. Note the benefits of complementary data.

ISOTOPIC TRACERS OF FLOW AND TRANSPORT THROUGH THE VADOSE ZONE*

Applications of environmental isotope tracers are complementary to conventional water-flow and solute-transport investigations. This is especially true in arid and semi-arid regions that are commonly characterized by extensive zones of unsaturated rock. Natural variations in the hydrogen and oxygen stable isotope ratios of water were first noted in the early 1950s (Friedman 1953; Epstein and Mayeda 1953). Since that time, a number of different isotopic methods have been developed for studying hydrologic problems, including groundwater flow and mixing, recharge areas of aquifers, subsurface residence times, and multi-phase reactive exchange of chemicals (Phillips 1995). In this section, a brief overview of several of the more commonly used isotopic techniques for tracking the movement of water through the vadose zone will be presented.

Hydrogen and Oxygen Isotope Ratios of Water

Craig (1961) found that the hydrogen (δD) and oxygen ($\delta^{18}O$) isotope ratios of most rainwater lie on or near a line of slope 8 on a plot of δD versus $\delta^{18}O$. This line is commonly referred to as the Global Meteoric Water Line (GMWL) and is shown in Figure 3-36. The relationship between δD and $\delta^{18}O$ for rainwater from a specific area relative to the GMWL is a function of a variety of factors, including the distance from the ocean, altitude, and temperature. In regions where there are large variations in the δD and $\delta^{18}O$ values of rainwater (for example, in the western United States), differences in the isotopic compositions of groundwater have been used to distinguish sources of recharge, flow directions, and groundwater mixing (see for example, Stahl *et al.* 1974; Hearn *et al.* 1989; Criss and Davisson 1996; Davisson *et al.* 1999).

The δD and $\delta^{18}O$ values of rainwater can also exhibit significant seasonal variations. This difference is most striking in arid or semi-arid regions, which are generally characterized by large temperature variations between summer and winter rainy seasons. These natural, seasonal changes in the isotope compositions of rainwater have been used in a number of studies to estimate infiltration rates (see for example, Phillips

*This section was contributed by Mark Conrad and Boris Faybishenko.

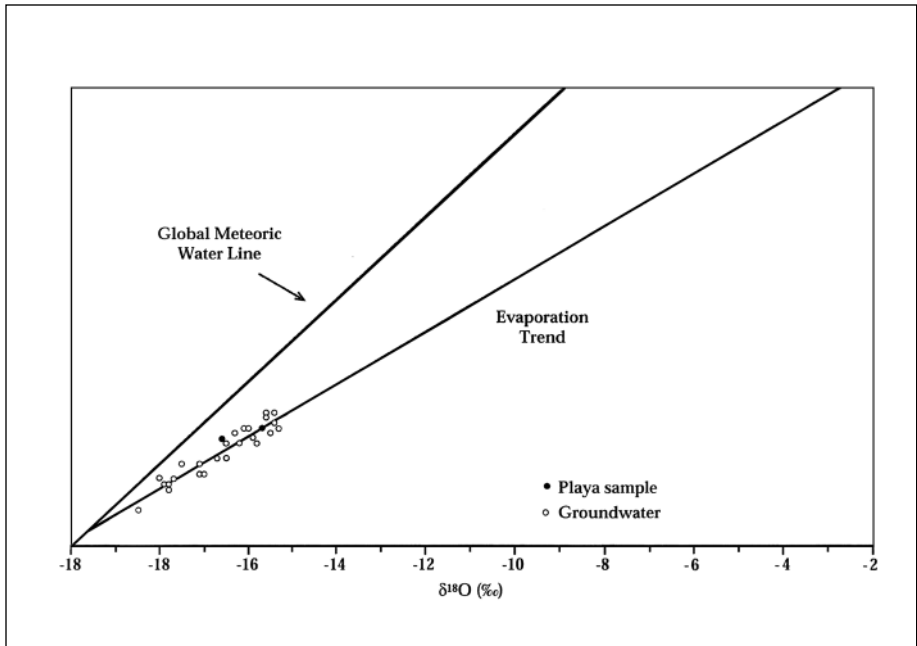


Figure 3-36. $\delta^{18}\text{O}$ and δD data for groundwater samples collected from monitoring wells at the TAN site of the Idaho National Engineering and Environmental Laboratory and from playas adjacent to the TAN site. Also shown are the global meteoric water line and a best-fit line through the data, which is equivalent to a typical trend of data observed for evaporated waters (Conrad *et al.*, 1999).

1994; Allison *et al.* 1994; Liu *et al.* 1995; Newman *et al.* 1997). However, water-vapor diffusion and isotopic exchange can attenuate these seasonal signals over relatively short time -scales, limiting the utility of these studies to relatively recent infiltration events.

The hydrogen and oxygen isotope ratios of surface waters can be altered if they undergo significant evaporation before they infiltrate into the subsurface. As water evaporates, lighter isotopes are preferentially separated into the vapor phase, and the residual water becomes enriched in D and ^{18}O . Depending on the humidity and temperature of an area, the slopes of evaporation trends on plots of δD versus $\delta^{18}\text{O}$ are generally between 3 and 6. The result is that highly evaporated waters will lie significantly off of the GMWL on δD - $\delta^{18}\text{O}$ plots. The distinctive isotopic compositions of evaporated surface waters can be used to track infiltra-

tion of those waters through the vadose zone (Gat *et al.* 1969; Gonfiantini *et al.* 1974; Komor and Emerson 1994; Gaye and Edmunds 1996). An example of this is given in Figure 3-36. At this site at the Idaho National Engineering and Environmental Laboratory in eastern Idaho, the isotope compositions of the groundwater have been significantly shifted by infiltration of strongly evaporated water from playa lakes. In addition to the natural evaporative process, waters with isotope compositions shifted by evaporation during industrial processes can also be used to identify and trace input of water from leaking tanks and pipes (Ingraham 1994).

It is also possible to use water artificially enriched in the heavy isotopes (D, ^{18}O) as tracers for studying infiltration through the unsaturated zone (Swenson 1997; Anderson *et al.* 1997). An advantage of using D_2O and H_2^{18}O is that they serve as direct tracers of water flow and are not affected by processes that can influence introduced solute tracers. Until recently, tracer studies using D_2O and H_2^{18}O have been limited by relatively time-consuming and expensive analytical procedures. However, recent advances in stable-isotope analytical techniques have greatly reduced the time and cost per analysis, and should lead to more widespread use of these isotopic tracers.

Dating Water Using Cosmogenic Radionuclides

Cosmogenic radionuclides are a special group of isotopes that have gained widespread use for dating soil water and estimating net infiltration rates through the vadose zone. These isotopes are naturally produced at low levels by interaction between cosmic rays and the atmosphere. The most widely used are ^3H , ^{14}C , and ^{36}Cl . Other cosmogenic radionuclides that deserve mention, but will not be discussed here, include ^{39}Ar (Loosli 1983) and ^{129}I (Fabryka-Martin *et al.* 1985).

In addition to natural production, above-ground testing of nuclear bombs during the 1950s and 1960s also produced ^3H , ^{14}C , and ^{36}Cl . For ^3H and ^{36}Cl , these increases were very large and dominate the natural signals in recent waters. Since above-ground testing was halted, the atmospheric levels have been dropping back to normal (pre-bomb testing) atmospheric levels. These signals have provided additional opportunities for tracking water movement in the vadose zone, especially on short time-scales.

^3H (tritium) has a relatively short half-life (12.4 years). Concentrations are measured in tritium units (TU) that correspond to 1 ^3H atom in 10^{183} hydrogen atoms (Libby 1971). The normal background concentration is low (between 2 and 10 TU). For these reasons, under normal circumstances, tritium is only useful for identifying an input of very recent water. However, tritium levels from nuclear testing reached >2000 TU in the northern hemisphere and >50 TU in the southern hemisphere, peaking during 1963-64. In the southern hemisphere, ^3H concentrations have already decayed to near pre-bomb atmospheric levels and are of limited use (Cook *et al.* 1994). In the northern hemisphere, the bomb pulse can still be clearly distinguished and has been used in numerous studies to date infiltration rates of recent waters (see for example, Chapman *et al.* 1992; Scanlon 1992). As with stable hydrogen isotope ratios, however, tritium signals can also be attenuated by vapor exchange that can smear out the bomb-pulse signal in the unsaturated zone.

^{14}C has a significantly longer half-life (5730 years) than ^3H and can be used to date much older events. The natural ratio of $^{14}\text{C}/\text{C}$ is 1.175×10^{-12} . During nuclear bomb testing, the concentration of ^{14}C only reached approximately twice its natural levels (Lehman *et al.* 1993). This level of ^{14}C does not overwhelm the natural signal, but should be considered when used to interpret transport of recent waters.

Using ^{14}C concentrations to date groundwater assumes that water infiltrating through the root zone will pick up dissolved inorganic carbon (DIC) from sources in equilibrium with the atmosphere (for example, from root respiration or decay of recent organic matter). Then, as the water infiltrates deeper into the soils, the DIC will remain with the water, allowing dating by radioactive decay. The most significant problem with using ^{14}C for studying transport in the vadose zone is its reactive nature. Shallow soils often contain relatively high concentrations of organic matter, some of which may be relatively old. If a significant amount of microbial degradation of “old” organic matter occurs along the infiltration pathway, this can lead to erroneously old ages for the waters. It is also possible that dissolution of soil carbonates or carbonate rocks in the subsurface can add significant amounts of old carbon to the DIC in the waters, leading to the determination of anomalously old ages. Finally, significant inputs of magmatic carbon (for example, in active volcanic or geothermal areas) can also yield old ages. It is

possible to recognize inputs of old carbon from some of these sources by measuring the stable carbon isotope ratios ($\delta^{13}\text{C}$ values) of the DIC or associated soil gas CO_2 (see below), but care should be taken in interpreting this data (Landmeyer *et al.* 1995; Johnson and DePaolo 1996).

^{36}Cl has the longest half-life (301,000 years) of these three tracers. During bomb testing in the mid-1950s, its atmospheric concentration increased to more than 1,000 times natural levels. Because of the long half-life, these concentrations do not change significantly over the short term (unlike tritium). Natural atmospheric concentrations of ^{36}Cl can vary considerably, based on latitude and proximity to coastal areas. Also, a variety of subsurface processes (including evapotranspiration, *in situ* production, and radioactive decay) can affect both the concentration of ^{36}Cl and the $^{36}\text{Cl}/\text{Cl}$ ratio.

^{36}Cl concentrations, when combined with chloride, ^{14}C , and ^3H concentrations, provide a powerful way of for quantifying infiltration rates through the vadose zone, origin of surface waters, erosion processes, and other hydrologic processes (Scanlon *et al.* 1990; Scanlon 1992; Cook *et al.* 1994; Murphy *et al.* 1996). In soil profiles of arid regions, high $^{36}\text{Cl}/\text{Cl}$ ratios (exceeding 9×10^{-12}) often appear at depths of 0.5-2 m from the surface (Philips 1994) resulting from slow migration of ^{36}Cl released from bomb pulse in the 1950s. Note that the background ratios of $^{36}\text{Cl}/\text{Cl}$ range from 0.5 to 1.5×10^{-12} in the western USA (Davis *et al.* 1998). The presence of bomb-pulse ^{36}Cl in deep waters at Yucca Mountain (the proposed high-level nuclear waste repository in Nevada), has significantly changed perceptions of the hydrology of the site, underscoring the potential role of fast pathways for infiltration of water through the vadose zone (Fabryka-Martin *et al.* 1993; Levy *et al.* 1997).

Reactive Isotope Tracers

Reactive isotopic tracers are those that can interact with the matrix to acquire its isotopic signature. They can be particularly useful for determining the nature of interaction between infiltrating fluid and specific subsurface features. Generally, oxygen and hydrogen isotopes are not considered reactive isotopes at low temperatures, but at higher temperatures (for example, in geothermal systems) they can be significantly shifted by interaction with the host rocks. The degree of shift can be used to estimate the minimum water to rock ratio in the system (for example, Taylor 1974).

At lower temperatures, the most sensitive isotopic tracers are those with low solubility in the water relative to their concentration in the matrix. Two examples of reactive isotope tracers are the $\delta^{13}\text{C}$ values of pore-water DIC and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of dissolved Sr. There are a number of other isotopic tracers that have been or could potentially be used to study infiltration and transport in the vadose zone (for example, the isotopic ratios of metals and radionuclides to track their movement through the vadose zone; McCarthy *et al.* 1998). However, we will focus here on carbon and strontium isotopes.

The stable carbon isotope ratios of DIC in vadose zone pore-waters are directly related to the $\delta^{13}\text{C}$ values of associated CO_2 . Their isotope compositions are the functions of factors such as the pH of the pore-fluids pH and the temperature (Wigley *et al.* 1978). Further, since CO_2 is a gas phase and is relatively mobile, it can be affected by exchange with the atmosphere (Cerling 1984). As discussed above, the general assumption is that pore-water DIC attains its carbon isotope composition in the relatively high CO_2 region within the root zone of surface soils. However, there are a number of other subsurface processes that can significantly affect the carbon isotope compositions of DIC/ CO_2 in the unsaturated zone and are direct indications that these processes are occurring in the subsurface. Examples include microbial degradation of hydrocarbon contaminants (Conrad *et al.* 1997) and interaction with subsurface carbonate units (Johnson and DePaolo 1996).

The strontium isotope ratio of dissolved strontium in water is very sensitive to interaction with the rock matrix, even at the relatively low temperatures characteristic of most groundwater systems. The concentrations of strontium in water are typically 1,000 times less than the concentrations in the rock. After relatively minor degrees of interaction with the matrix, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the water will quickly become dominated by the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the rock. The length-scale of this change can be used to calculate factors such as the flow velocity of the fluids and/or the relative amounts of water and rock in the system (Johnson and DePaolo 1997a, b).

CHARACTERIZATION AND MONITORING FOR BIOREMEDIATION*

Characterization and monitoring of bioremediation can be as simple as maintaining a fermentor for above-ground processes like prepared

*This section was contributed by Terry Hazen.

beds, land farming, bioslurry reactors, composting, and bioreactors. The terrestrial subsurface is much more difficult because of sampling problems, poorly defined interfaces, and spatial heterogeneity. For any type of bioremediation, careful consideration and planning must be given to the remediation objectives, sampling, the types of samples, frequency, cost, priority, and background literature for method verification. The microbiology and chemistry may be of less overall importance to the remediation of the site than the hydrology, geology, meteorology, toxicology, and engineering requirements. All of these things must be integrated into the plan for characterization and monitoring of any site. For examples of test plans for bioremediation, see Hazen *et al.* (1991), Lombard and Hazen (1994), and Nelson *et al.* (1994).

The type of sample used for monitoring and characterization of sediment or groundwater can have a significant impact on a bioremediation project. Fortunately, most bioremediation applications are shallow and eutrophic, owing to the nature of the waste mix usually deposited. Enzien *et al.* (1994) further underscored the need for careful sampling when they showed significant anaerobic reductive dechlorination processes occurring in an aquifer whose bulk groundwater was aerobic (greater than 2 mg/L O₂).

It is extremely difficult to determine the rate and amount of contaminant that is bioremediated in any environment. Many of the problems and measurements discussed above for mass balance also apply here.

In recent years, bioremediation studies have focused on the measurement of biodegradation products rather than organisms, due to the difficulty in measuring organisms. Soil and groundwater measurements of microorganisms often require long incubations or long preparation times, and the measurements are usually not specific to contaminant-degraders. Several methods have been used to determine the rate and amount of biodegradation: monitoring of conservative tracers, measurement of byproducts of anaerobic activity, intermediary metabolite formation, electron acceptor concentration, stable isotopic ratios of carbon, and the ratio of non-degradable to degradable substances. Helium has been used at a number of sites as a conservative tracer since it is non-reactive and non-biodegradable, and moves like oxygen (National Research Council 1993). By simultaneously injecting He with O₂ at

known concentrations and comparing the subsurface ratios over time, the rates of respiration can be calculated. This technique has also been used to measure rates of injected methane consumption (Hazen 1991). Bromide has been successfully used as a conservative tracer for liquid-injection comparisons with nitrate, sulfate, and dissolved oxygen (National Research Council 1993). By-products of anaerobic biotransformation in the environment have been used to estimate the amount of biodegradation that has occurred in anaerobic environments, (for example, PCB-containing sediments). These byproducts include methane, sulfides, nitrogen gas, and reduced forms of iron and manganese (Harkness *et al.* 1993). Measurements of chloride changes have also proven useful in indicating the amount of chlorinated solvents that have been oxidized or reduced (Hazen *et al.* 1994). Consumption of electron acceptors (O_2 , NO_3 , or SO_4) has been used for measuring rates of biodegradation and bioactivity at some bioremediation sites (National Research Council 1993; Smith *et al.* 1991). Bioventing remediations of petroleum-contaminated sites rely on stable isotopic ratios of carbon, carbon dioxide production, and oxygen consumption to quantify biodegradation rates in the field (Hinchee *et al.* 1991; Hoepfel *et al.* 1991). Mixtures of contaminants (for example, petroleum hydrocarbons) can have their own internal standards for biodegradation. By comparing concentrations of nonbiodegradable components of the contaminant source with concentrations of degradable components from both virgin and weathered sources, the amount of degraded contaminant can be calculated. These measurements have been used on the Exxon Valdez spill cleanup (Glasser 1994) and at a number of other petroleum-contaminated sites (Breedveld *et al.* 1995).

Microbial ecologists have continually struggled with methods to identify the organisms in the environment, and to measure how many organisms are present and how active they are. For bioremediation, we need to know what contaminant-degraders are present, how many are present, and how active they are. We may also need to know if there are other organisms in the environment that are important in the biogeochemistry, and what proportion of the total community the degraders represent.

Plate counts can only provide a measurement of what microbes are present in the sample that will grow on the media used, under the conditions incubated. Since the number of possible media and possible incubations are infinite, the number of possible interpretations is also infinite. Generally, heterotrophic plate counts have been used to show that bacteria densities in the sediment or groundwater increase in response to biostimulation (Litchfield 1993). Using contaminant-enrichment media and either plates or most probable number (MPN) extinction dilution techniques, the number of contaminant-degraders can be estimated (National Research Council 1993). However, serious fallacies appear in the underlying assumptions of many of these assays. For example, diesel-degraders are determined using minimal media with a diesel-soaked piece of cotton taped to the top of the petri dish. In such a situation, it is unclear whether the colonies that are observed are using the diesel, or whether they are merely tolerant of the volatile components of the diesel fuel. MPN assays have also been used to conservatively measure methanotroph densities in soil and groundwater at chlorinated solvent-contaminated sites. These measurements involve sealing each tube under an air/methane headspace and then scoring positive only those tubes that are turbid and have produced carbon dioxide and used methane (Fogel *et al.* 1986). The incubation time for plate count and MPN contaminant-degrader assays is 1 to 8 weeks, thus negating their use for real-time monitoring and control.

A number of direct-count assays have been tried on contaminant degraders including direct fluorescent antibody (DFA) staining, acridine orange direct counts (AODC), and fluorescein isothiocyanate (FITC) direct counts. The fluorochrome stains only indicate the total number of organisms present in the sample; they do not indicate the type of organism or its activity. However, these techniques have been used in bioremediation studies to determine changes in the total numbers of organisms (Litchfield 1993). Increases in total counts have been found when contaminated environments are biostimulated. DFA shows promise but requires an antibody that is specific to the contaminant-degraders in that environment. The environment must be checked for organisms that may cross-react with the antibody and for contaminant-degraders that do not react with the antibody. DFA will be most useful in monitoring specific organisms added for bioaugmentation, though it has been used in biostimulation applications (Fliermans *et al.* 1994). Since the

assay time is only hours for these direct techniques, they have significant advantages for real-time monitoring and rapid characterization.

Biological activity at bioremediation sites has been determined in a number of ways: Iodophenyl-Nitrophenyl, Tetrazolium (INT) Chloride activity/dehydrogenase, fatty acid analyses, acetate incorporation into lipids, ^3H -thymidine incorporation into deoxyribonucleic acid (DNA), BIOLOGTM, phosphatase, and acetylene reduction. The INT test has been used in combination with direct counts since INT-formazan crystals can be detected in the cell. Cells with crystals are assumed to be actively respiring since the reaction occurs at the electron transport system of the cell. The assay requires only a 30-minute incubation; however, it can only be used in groundwater samples since particles in sediment samples cause too much interference with interpretation of the intracellular crystals. Barbaro *et al.* (1994) used this technique to measure microbial biostimulation of the Borden Aquifer in Canada.

Phospholipid fatty acid (PLFA) analyses have been used for characterization and monitoring at a number of bioremediation sites. An organism's PLFAs (signature compounds) may be unique to its species or even its strain, or the PLFAs may be conserved across physiological groups, families, or even kingdoms. Certain groups of fatty acids (cis and trans isomers) may also change in response to the physiological status of the organism. PLFAs have been used at bioremediation sites to provide direct assays for physiological status (cis/trans ratio), total biomass estimates; and presence and abundance of particular contaminant-degraders and groups of organisms, such as methanotrophs, actinomycetes and anaerobes (Phelps *et al.* 1989; Heipieper *et al.* 1995; Ringelberg *et al.* 1994). PLFAs would seem to be a panacea for characterization and monitoring of bioremediation. Unfortunately, the assays require -70°C sample storage and long extraction times, they have a fairly high detection limit (10,000 cells), and they require expensive instrumentation. Nevertheless, this technique merits careful consideration since it is a direct assay technique and is so versatile.

Radiolabeled acetate and thymidine incorporation into lipids and DNA, respectively, have been used at bioremediation sites to provide measurements of total community metabolic and growth responsiveness (Fliermans *et al.* 1988; Palumbo *et al.* 1995). These techniques require incubation, extraction, purification, and radiolabeled substrates, making interpretation of results difficult.

The BIOLOGTM assay has also been adapted to determine the activity of bacteria (with regard to contaminants) in groundwater and soil samples. The assay consists of a 96-well titer plate with carbon sources and an electron transport system indicator. It can be used to identify isolates (pure cultures of one organism separated from the community) and to examine the overall activity of a soil or water sample of a particular substrate. Gorden *et al.* (1993) adapted the assay to determine activity of different contaminants by using both contaminants and the electron transport system (ETS) indicator alone and adding contaminants to the plates with substrates to determine co-metabolic activity. The assay provides more rapid screening than other viable count techniques, but it suffers from some of the same problems, such as incubation conditions and repeatability. It is also difficult to determine if the contaminants are being transformed or tolerated.

Phosphatase and dehydrogenase enzyme assays have also been used to access bioactivity in soil and groundwater during bioremediation of terrestrial subsurface sites. Acid and alkaline phosphatase have been linked to changes in ambient phosphate concentrations and bioactivity at contaminated sites caused by biostimulation (Lanza and Dougherty 1991). The incubation, extraction, and interference caused by pH differences in samples make results difficult to interpret. Acetylene reduction has been used to indicate nitrogenase activity in a few bioremediation studies; however, the importance of nitrogen fixation for most bioremediation is probably insignificant, unless the site is oligotrophic, e.g. very low in nutrients (Hazen *et al.* 1994).

Nucleic acid probes provide, at least theoretically, one of the best ways to characterize and monitor organisms in the environment (Hazen and Jiménez 1988; Brockman 1995). Since many contaminants, especially the more recalcitrant ones, are degraded by only a few enzymes, it is possible to produce DNA or even ribonucleic acid (RNA) probes that will indicate the amount of that gene in the environment. This quantity reveals whether the functional group that can degrade or transform the contaminant is present, and if so, indicates its relative abundance. Since probes have also been found for species, families, and even kingdoms, soil and groundwater communities can be monitored. Recently, conserved regions in ribosomes have also been found, allowing samples to be probed for the relative abundance of ribosomes and, hence, the bioactivity of the total community (Ruminy *et al.* 1994). Bowman *et al.*

(1993) demonstrated that probes for methanotrophs indicated their presence in soil at trichloroethylene (TCE)-contaminated sites in South Carolina and Tennessee. Brockman *et al.* (1995) also showed that methane/air injection at the South Carolina site increased the methanotroph probe signal in sediment near the injection point in the aquifer. The probe-signal increases for methanotrophs coincided with increases in the MPN counts for methanotrophs. Table 3-16 summarizes bioremediation characterization and monitoring parameters.

TABLE 3-16 Bioremediation Characterization and Monitoring Parameters

Measurements	Parameter
Biomass	
Viable Counts	Plate counts, Most Probable Number (MPN), enrichments, BIOLOG™
Direct Counts	Acridine Orange Direct Count (AODC), Fluorescein Isothiocyanate (FITC), Direct Fluorescent Antibody (DFA)
Signature Compounds	Phospholipid Fatty Acid (PLFA), DNA, RNA
Bioactivity and Bioremediation	
Daughter Products	Cl, CO ₂ , CH ₄ , stable isotopic C, reduced contaminants
Intermediary Metabolites	Epoxides, reduced contaminants
Signature Compounds	PLFA, ribosome probes, BIOLOG™, phosphatase, dehydrogenase, Iodophenyl-Nitrophenyl, Tetrazolium Chloride (INT), acetylene reduction, recalcitrant contaminants
Electron Acceptors	O ₂ , NO ₃ , SO ₄ , (microrespirometer)
Conservative Tracers	He, CH ₄ , Cl, Br
Radiolabeled Mineralization	¹⁴ C, ³ H -labeled contaminants, acetate, thymidine
Sediment	
Nutrients	PO ₄ NO ₃ , NH ₄ , O ₂ , total organics, SO ₄
Physical/Chemical	Porosity, lithology, cationic exchange, redox potential, pH, temperature, moisture, heavy metals
Toxicity	Microtox™, Mutatox™

Thus, sediment can be directly extracted and probed with DNA and RNA for bioremediation characterization and monitoring. As more nucleic acid sequences are found and mapped, it will be possible for us to construct sequences that will detect the amount of a gene from any organism in that environment involved in the desired transformation of the contaminant. Clearly, this ability will allow bioremediation injection strategies to have better control of the process in terms of effecting the desired changes in the functional group responsible for the bioremediation process. Unfortunately, nucleic acid probe technology has some serious obstacles to overcome before it becomes practical:

- The direct detection of nucleic acids in soil and groundwater requires lysis, extraction, and purification
- Soil humics and groundwater pH interfere with the nucleic acid signal
- The detection limit for most probe assays is 10,000 cells.

The extraction and purification steps also significantly increase the cost and analysis time. These problems are not insurmountable, but will impede realistic use of nucleic acid probes for bioremediation. Certainly, research in this area needs to be encouraged, given the sound theoretical advantages that these techniques provide for bioremediation.

DETERMINATION OF UNSATURATED HYDRAULIC PROPERTIES OF VARIABLY SATURATED SOILS AND ROCKS*

The unsaturated hydraulic properties of porous media are the water-retention and unsaturated hydraulic-conductivity functions that are the constitutive relationships of the Richards' equation for unsaturated flow in the vadose zone:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left[K(h) \left(\frac{\partial h}{\partial z} + 1 \right) \right] \quad (3.10)$$

*This section was contributed by F.J. Leij and B. Faybishenko.

where h is the soil-water pressure head, θ is the volumetric water content, K is the unsaturated hydraulic conductivity—which can be expressed as a function of either h or θ , t is time, and z is the vertical distance (coordinate) taken positive upward.

The soil-water retention curve, $\theta(h)$, quantifies the ability of a soil to retain water by relating the soil-water content to the soil-water pressure head. The latter expresses the soil-water energy status. The soil-water content can also be expressed in terms of the effective water saturation (S_e). Some theoretical concepts of the soil-water energy status given in terms of the matric potential, soil-water suction, and the soil-water matric are discussed in Chapter 1. Experimental methods to determine both water saturation and matric potential are discussed in the section “Field Vadose Zone Characterization and Monitoring Methods,” above.

The unsaturated hydraulic-conductivity function quantifies the ability of an unsaturated soil to transmit water under different saturations, by relating the hydraulic conductivity to either the pressure head, $K(h)$, or the water saturation, $K(S_e)$. Because this function is nonlinear, it renders Richards’ equation nonlinear. Soil hydraulic properties can be determined using a variety of experimental field and laboratory methods, and can also be estimated with indirect methods, using different empirical and semi-empirical approaches (Klute, 1986; van Genuchten *et al.* 1992; 1999).

FACTORS AND PROCESSES AFFECTING HYDRAULIC PARAMETERS

The water-retention and hydraulic-conductivity functions are strongly affected by both the texture and structure of soils as well as by the physical and chemical properties of the fluids (typically air and water) occupying the pore space. Numerous investigations have attempted to elucidate how hydraulic properties depend on particle- and pore-size distributions, clay content, shrinkage and swelling phenomena, entrapped air, temperature, solution composition, and other physical and chemical properties of soil and soil solution.

Figure 3-37 shows a schematic of soil water retention curves (SWRCs) exhibiting hysteresis for a typical coarse-textured soil (Luckner *et al.* 1989). Both conductivity and retention functions are hysteretic under wetting and drying conditions. Variations in hydraulic properties affected by hysteresis, soil heterogeneity, preferential flow, soil contam-

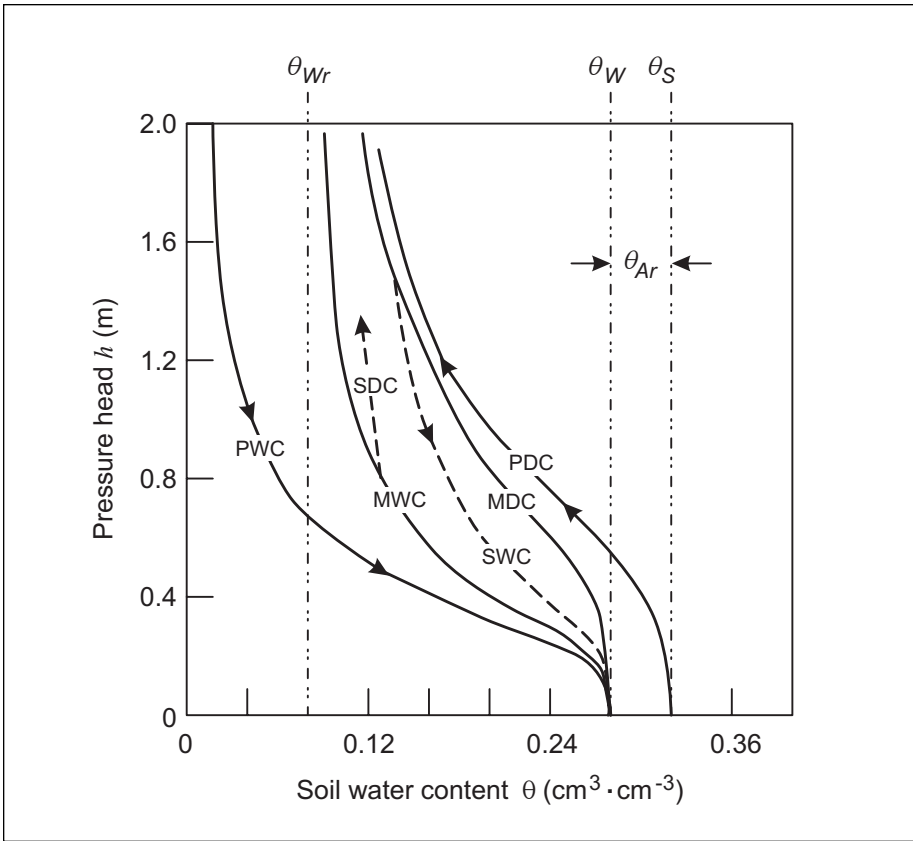


Figure 3-37. Hysteresis of the SWRC for a coarse-textured soil (Luckner *et al.* 1989). PDC is the primary drainage curve, PWC is the primary wetting curve, MDC is the main drainage curve, MWC is the main wetting curve, SWC is the scanning wetting curve and SDC is the scanning drainage curve.

ination, and air entrapment are of particular interest in predicting the effect of remediation activities.

Soil Heterogeneity and Preferential Flow

The natural spatial variability of soils physical properties causes hydraulic conductivity to vary by as much as several orders of magnitude over short distances. The heterogeneity of natural soil samples

makes it difficult to evaluate the methods used to determine hydraulic properties because results are not accurate and/or reproducible. An additional complication is that different wetting and drying events during experiments create a multitude of spatial water-content distributions and preferential flow, which may result in nonuniqueness of hydraulic properties (Topp *et al.* 1980, Topp and Davis 1985; Smiles *et al.* 1971; Faybishenko 1986; Globus 1987; Plagge *et al.* 1999).

Flow through macropores and cracks in structured soils creates preferential flow, especially under near-saturated and saturated conditions. Unfortunately, it is very difficult to accurately and reproducibly measure the hydraulic properties of a soil at low suctions (that is, close to saturation). Conventional methods for estimating hydraulic properties, which are suitable for capillary flow in the soil matrix, should be supplemented with techniques to quantify noncapillary flow in macropores. One approach assumes that the medium consists of several pore structures, and the hydraulic properties of the medium are obtained by summing the properties for individual structures (Ross and Smettem, 1993; Durner 1994). An example is provided by Mohanty and van Genuchten in the case study on the accompanying CD “Field and Modeling Studies of Preferential Flow in Macroporous Soils.” Mohanty and van Genuchten determined the relative trend of soil-water retention and hydraulic- conductivity functions near saturation and established piecewise-continuous functions to take into account preferential flow through macropores. These hydraulic functions were then used to predict field-scale flow and transport in a flood-irrigated field at Las Nutrias, New Mexico.

Another type of preferential flow is fingering, which results from wetting-front instabilities. A well-known scenario for water fingering involves infiltration of water from a fine-textured soil horizon overlying a coarse-textured horizon (Hill and Parlange 1972; Parlange and Hill 1976). Initially, water in the smaller pores of the topsoil cannot enter the larger pores of the subsoil because of insufficient soil-water suction developed in the coarser material (the coarser subsoil has a lower air entry and a higher “water” entry value than the topsoil). Lateral flow will occur until the pressure is sufficient for water to enter the subsoil. Because the coarser subsoil can transmit a larger water flux than the topsoil, water flow in the coarser subsoil is confined to a number of fingers.

Other possible factors leading to water fingering involve air entrapment, hydrophobicity, changes in interfacial tension, increased water content with depth, continuous low-rate irrigation, and lenses of coarse soil acting as a capillary barriers (Raats 1973; Diment *et al.* 1982; Glass *et al.* 1989; Kung 1990a, b; Ritsema and Dekker 1995).

Entrapped Air

Air entrapment occurs when the air phase is discontinuous and is no longer connected to the atmosphere. Air remains as small, partly immobilized, disconnected bubbles, which can behave like solid spheres. Air can be entrapped in both dead-end and open pores. Entrapped air may reduce the soil's hydraulic conductivity by as much as two orders of magnitude (Faybishenko 1986, 1995, 1999a). Hysteresis of water retention curves may also be affected by air entrapment (Chahal 1965; Faybishenko 1983; Hopmans and Dane 1986; Kaluarachchi and Parker 1987; Stonestrom and Rubin 1989a, b).

Effect of Salinity and Contaminants

Chemical compounds dissolved in the aqueous phase can affect the hydraulic properties in several ways. Firstly, the solution chemistry may affect surface tensions (that is, the interfacial tension and contact angle, which are parameters in the Laplace-Young equation). Dissolved organic compounds tend to lower surface tension while ionic species, at high concentrations, may increase the surface tension. Sorption of chemical compounds by the solid may alter the contact angle, that is, the wettability of the solid. Demond *et al.* (1994) and Lord *et al.* (1997) determined changes in the capillary pressure in the presence of solutes. Demond *et al.* (1999) investigated the impact of speciation, sorption, and partitioning on the relationship between the primary drainage capillary pressure and saturation. For an aqueous system containing octanoic acid, lowering the pH below the pKa of 4.8 transformed the anionic into a neutral form of the acid. The corresponding decrease in surface tension resulted in a lowering of the soil-water pressure head. For a two-liquid medium containing o-xylene and water, lowering the pH led to preferential partitioning of the neutral compound into the o-xylene phase and a corresponding increase in capillary pressure. Furthermore,

sorption of cetyltrimethyl ammonium caused the solid to become hydrophobic (increase in the contact angle beyond 90°) and lowering of capillary pressure. However, these processes are not well understood at this time.

Secondly, the pore geometry may be altered. Such changes may be attributed to changes in solution composition (that is, dispersion and flocculation), or changes in hydraulic regime (that is, shrinking and swelling). The detrimental effects of soil salinity on hydraulic conductivity of soils have been well-documented (Ghassemi *et al.* 1995). The pH is an important factor, affecting the charge distribution of clay particles. If the electrolyte level is low enough, depending on the type of cations, the repulsion of particles and the collapse of soil aggregates cause dispersion and changes in pore geometry. Furthermore, small particles may be dislodged and clog downstream pores. The inverse process of flocculation occurs when the electrolyte level is increased or if the cationic composition is changed (for example, during the displacement of sodium by calcium cations). Flocculation and aggregation are also promoted by a heterogeneous charge distribution across the soil particles. The negative faces of clay platelets and positively charged edges of other platelets attract each other to form a stable aggregate. However, the positive charge is highly variable, and an increase in pH or the addition of polyanions such as phosphates can lead to dispersion. Swelling and shrinking phenomena may occur during imbibition or release of water from the soil. Several scales of shrinking may be discerned, such as crystalline and osmotic swelling (Parker 1986). It is important that the swelling process will usually not be irreversible. Although the redistribution of soil colloids is not totally random, the complexity of the flow field and driving forces for colloids makes a physical description of the process rather difficult.

Numerous publications have been devoted to the influence of soil salinity on hydraulic properties. Shainberg and Levy (1992) and Lima *et al.* (1990), among others, reported an increase in water retention for relatively higher amounts of sodium. The behavior of the saturated conductivity as a function of salinity and pH were investigated by Rhoades and Ingvalson (1969) and Suarez *et al.* (1984), respectively. McNeal and Coleman (1966) demonstrated that the saturated hydraulic conductivity is reduced for lower total electrolyte concentrations and higher sodium levels. There are various mechanisms that contribute to this

reduction in conductivity. Swelling will change the soil structure, soil pores may be partially or completely blocked (Quirk and Schofield 1955), and dispersion may result in movement of clay platelets, causing clogging of (smaller) soil pores, and consequently reducing the conductivity (cf. Shainberg and Levy 1992).

Temperature Effects

Soils near the land surface can experience diurnal and seasonal temperature fluctuations of as much as 50°C. Soil temperature affects fluid properties, including water density, viscosity, and surface tension as well as gas density, viscosity, and saturation vapor pressure. It also affects the contact angle, which, in turn, affects soil hydraulic properties. Ambient temperature affects evaporation from the surface, and the soil temperature fluctuations influence affect the intra-soil evaporation and condensation of water. Condensed water may become an important source of infiltration in the vadose zone in arid and semi-arid areas. Temperature gradients will act in different ways on water and vapor flow. Simulations of nonisothermal water flow and solute transport should consider the energy transfer and the effect of temperature on constitutive soil hydraulic parameters as well as solute-transport parameters.

It is important to consider the effect of temperature for several practical applications. At high-level radioactive waste disposal sites (for example, at Hanford), radioactive decay generates significant thermal energy. This, in turn, will change the soil and rock transport properties in and around the repository. Thermal extraction methods, often used to enhance petroleum recovery from reservoirs, are now being applied to improve the removal of nonaqueous phase liquid contaminants from the subsurface (Price *et al.* 1999; Udell 1998). Prediction of the performance of these remediation methods requires incorporation of the effects of temperature on the pertinent soil hydraulic properties (She and Sleep 1998).

To determine the effect of temperature on the capillary pressure, Grant and Salehzadeh (1996) found that the ratio $P_c/(dP_c/dT)$ was a linear function of temperature with a slope equal to 1. Faybishenko (1983) experimentally determined that the ratio dP_c/dT is equivalent to $0.008P_{10^\circ\text{C}}$, where P_c is the matric potential in kPa, and T is the temper-

ature ($^{\circ}\text{C}$). A temperature change of 10°C causes a change in the pressure of 0.8 kPa. These data can be incorporated in the water-retention functions used in modeling (Grant and Salehzadeh 1996)

Instrumentation

The results of both field and laboratory determination of hydraulic properties depend on the type of instrumentation used. In particular, water-retention and unsaturated hydraulic-conductivity functions may depend on the flow geometry (axial, radial, or centrifugal) in laboratory cores as well as the magnitude and type of boundary conditions used to change the water content and pressure head during the experiment. Experimental methods are reviewed in detail by Klute (1986), Dirksen (1991), and Gee and Ward (1999).

Field Methods

Field methods are employed to observe flow and transport processes under natural conditions. *In situ* methods allow one to minimally disturb the soil profile and obtain realistic field-scale observations. However, these methods are time-consuming, difficult to implement, and frequently constrained to a narrow range of changes of saturation and water- pressure changes over the period of observations. Field results may be less accurate and reproducible than laboratory results, because of difficulty in controlling boundary conditions. A description of several field methods is presented below.

Instantaneous Profile Method

The instantaneous profile or unsteady drainage-flux method is used to determine the hydraulic conductivity by observing the water content and pressure head of a soil profile after the soil has been wetted (for example, by irrigation). Mass-balance calculations based on Richards' equation yield the hydraulic conductivity, whereas the observations of the water content and water pressure directly provide the water retention functions (Rose *et al.* 1965; Cassel 1974). The method is only applicable to well-drained soils with no significant lateral flow. There are several variations of the method (Green *et al.* 1986).

After the entire profile is wetted by ponding or irrigation, the soil can be covered to prevent evaporation. Arya *et al.* (1975) modified the method by using a zero-flux plane to allow evaporation. Pressure-head gradients are obtained by installing tensiometers at a sufficient number of depths. The water content profile is monitored using a neutron probe or TDR. The hydraulic conductivity at an arbitrary distance $z=L$ may be determined numerically by integrating the Richards equation:

$$\frac{\partial}{\partial t} \int_0^L \theta(z,t) dz = K(h) \frac{\partial H(z,t)}{\partial z} \bigg|_{z=L} \quad (3.11)$$

The main problem in interpreting the results of this method is the discrepancy between the location and scale of observation for pressure heads and water contents (Flühler *et al.* 1976). The solution of equation (3.9) using the finite-difference method may yield inaccurate or even negative values for the unsaturated hydraulic conductivity (Jury *et al.* 1991). Flühler *et al.* (1976) determined that in wet soils, the relative errors of hydraulic conductivity are approximately 20 to 30 percent, and for dry soils the errors may exceed 100 percent. The errors are greater for low hydraulic gradients (less than 0.3) and at earlier stages of the infiltration experiment. Plagge *et al.* (1999) determined that higher hydraulic gradients cause preferential, accelerated flow and decrease the tortuosity effect, thereby increasing the calculated hydraulic conductivity.

Numerical inverse procedures are now available that allow greater flexibility of the initial and boundary conditions, as well as can take into account the locations of pressure-head and water-content measurements (cf. "Inverse Methods," below).

Gravity Drainage Experiments

The gravity drainage or simplified unsteady drainage-flux method is a modification of the instantaneous profile method. However, the method assumes that gravity is the dominant force for water flow and that a unit hydraulic gradient exists (Sisson 1987). Under such conditions, it is not necessary to monitor the soil-water pressure head, and the conductivity function, $K(\theta)$, can be readily obtained from water-content observations. The unit gradient assumption is a severe one, but reason-

able for a deep vadose zone (Faybishenko 1986). Sisson (1987) and Sisson and van Genuchten (1991) proposed using the unit gradient water-flow models to fit the analytical functions for $dK/d\theta$ to the estimates for $dK/d\theta$ derived from field-measured water contents. Sisson and van Genuchten (1991) formulated the instantaneous profile data analysis in the form of a parameter optimization process. Application of the gravity-drainage analysis to the heterogeneous soils requires the use of a scaling procedure to transform the heterogeneous soil profile into an equivalent homogeneous soil profile (Shouse *et al.* 1991).

Ring Infiltrometry

Elrick and Reynolds (1992a) and Reynolds (1993) used analyses of three-dimensional, variably saturated flow to measure soil hydraulic properties, using a single-ring infiltrometer known as the Guelph Pressure Infiltrometer (GPI). Cylindrical infiltrometers have long been used to determine infiltration rate and saturated conductivity for essentially one-dimensional problems by using an inner and an outer ring (Bouwer 1986). An analytical solution equivalent to the expression by Wooding (1968) is fitted to the observed infiltration rate to determine the saturated conductivity. A very similar approach is followed to determine the conductivity with a well permeameter, where water is maintained at a constant level in a borehole, or by determining the sorptivity from the infiltration rate (Talsma 1969).

In the case of the GPI, a single ring (usually 0.10 m in diameter) is inserted approximately 0.02 to 0.05 m into the soil, and a Mariotte reservoir is used to supply water. The steady water flow rate through the ring is used to calculate the field-saturated hydraulic conductivity and matric flux potential. Parkin *et al.* (1999) reviewed some recent advances in the analysis of single-ring infiltrometer data, including the use of TDR results, which may improve experimental results in heterogeneous and low-permeability materials.

The steady-state constant-head/falling-head procedure is a refinement of the previous method (Elrick *et al.* 1992a, b). After establishing steady infiltration by maintaining a constant ponded head in the ring, the head is allowed to fall and is monitored as a function of time. An approximate analytical solution is then fitted to the observed head values to determine the field-saturated hydraulic conductivity and the matric flux potential

of the soil. This method is less sensitive to soil heterogeneities because head values are used for many different times.

The early-time constant-head/falling-head analysis is similar, except that it is not necessary to attain steady infiltration, which can take a significant amount of time to achieve in low-permeability soils (Elrick *et al.* 1995). The analysis is based on the assumption that early-time constant head infiltration into low-permeability, capillary-dominated materials is linear with the square root of time. This method can be useful for clay soils, landfill caps and liners, and waste water impoundments (Fallow *et al.* 1993; Elrick *et al.* 1995).

Tension Infiltrometry

Tension infiltrometers allow the determination of unsaturated hydraulic parameters with minimal disturbance of the soil. A circular, porous plate is placed on the soil surface, with a good hydraulic contact between plate and soil. The plate is connected to a Mariotte reservoir to provide a water supply under constant suction to the soil. The experiment is repeated for different water suctions. The experimentally determined infiltration rate is used to optimize the hydraulic parameters. The tension infiltrometry can be used to determine the soil sorptivity from the infiltration rate and the soil water diffusivity from the advance of the water front (Clothier and White 1981). More recent analyses rely on parameterization of the hydraulic properties. The hydraulic conductivity may be estimated from formulae developed for the initial transient or the final steady phase of infiltration (Reynolds and Elrick 1991; White and Perroux 1989).

Inverse numerical methods based on using observed infiltration-rate data, soil-water-content, or pressure-head data as well as soil water content or pressure head can be used to estimate parameters for both water-retention and hydraulic-conductivity functions. Wang *et al.* (1998) combined tensiometer and TDR data with tension infiltrometry results for different disk sizes. It should be noted that tension infiltrometry allows one to obtain precise flow-rate measurement in soils near saturation, which is needed to assess the unsaturated hydraulic parameters for macroporous soils (Mohanty *et al.* 1994).

Crust Method

Using a crust method (Hillel and Gardner 1970; Bouma *et al.* 1971), a steady soil water flux is established by applying water at a relatively low rate, that is, below the saturated conductivity, to a soil pedestal through a crust such as a puddled soil material, hydraulic cement (Bouma *et al.* 1983), or gypsum or silica sand (Bouma and Denning 1972). Because of the low hydraulic conductivity of the crust, the soil is unsaturated below the crust. The soil's unsaturated hydraulic conductivity function, $K(h)$, is calculated using the flow rate and the water pressure head distribution measured in soils with tensiometers. Crusts of different hydraulic conductivity are used to obtain various points of the $K(h)$ curve. (It is recommended to start the experiment with the crust of a lowest hydraulic conductance.) For a layered soil profile, tensiometers may be required for each layer. The method is more laborious compared to tension disk infiltrometry, but it has the advantage of maintaining one-dimensional flow within the soil pedestal.

Large Columns

Large columns of at least 3 m in length may be designed in the field for *in situ* determination of unsaturated hydraulic properties. An example of such a column is shown in Figure 3-38. The column can be instrumented with tensiometers, TDR probes, piezometers, temperature and salinity sensors, suction cups, and other devices to allow a thorough investigation of water flow and chemical transport.

Single Tensiometer Experiments

The unsaturated hydraulic conductivity of soils can be determined by applying suction to the interior of the tensiometer and measuring the water flux into (or out of) the tensiometer from the soil, a process that will decrease the volume of air in the tensiometer and increase the air pressure. Using this method, Timlin and Pachepsky (1998) developed a way of calculating unsaturated conductivity using a two-dimensional finite-element model (2DSOIL), coupled with a Marquardt-Levenberg algorithm to fit the calculated fluxes to the measured fluxes.

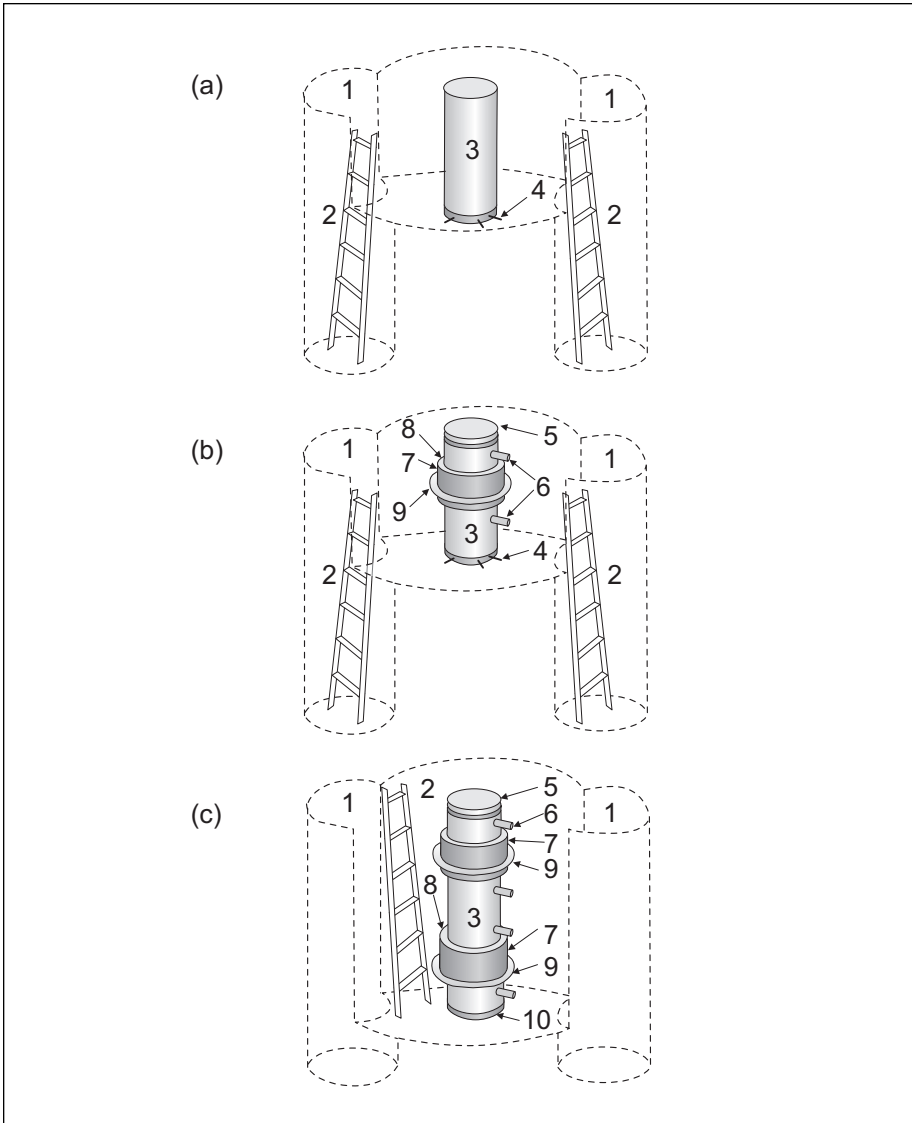


Figure 3-38. Sketch showing a field procedure of the preparation of a large vertical core between two boreholes (1) with ladders (2): (a) Upper segment (3) of uncovered core with cylindrical knife (4), (b) Upper segment is covered with top plate (5) and instrumented by probes (6) - tensiometers, piezometers and thermometers; the core is supported by backfill (7) placed between the core (3), cover (8), and platform (9), and (c) the sample has been cutoff, equipped with a bottom plate (10) (Faybishenko 1995)

LABORATORY METHODS

Laboratory determination of unsaturated hydraulic properties has many advantages over field methods, because boundary conditions and thermal regime can be carefully and easily controlled over a wider range of saturations. Laboratory results are also likely to be more accurate and reproducible. On the other hand, the laboratory soil-core volume tends to be smaller, and consequently a large number of soil cores are needed to adequately characterize a field site. Furthermore, sampling and handling of soil cores may inevitably affect the soil structure. Note that it is difficult to take soil samples of a loose structure and containing coarse materials such as pebbles and gravel. Because of the effect of instrumentation and expected changes in the soil structure, it is advisable to use several laboratory methods to determine hydraulic properties for a particular range of soil- water pressures.

Water Retention

The following contains a brief overview of methods to determine the water-retention function. Note that the previous section, “Field Vadose Zone Characterization and Monitoring,” and publications by Klute (1986) and Gee and Ward (1999) include the techniques needed to measure the two variables used in assessing the retention-curve function: the soil-water content and matric potential.

The water-retention function for the matric pressure above approximately -80 kPa can be determined by regulating suction in a cell apparatus containing the soil sample. Figure 3-39 shows a schematic of a suction cell apparatus. A saturated soil sample is placed on a porous plate or membrane to which a hanging water column is attached for control of the soil matric pressure. By automatically monitoring the outflow, the method offers a convenient and accurate procedure to determine water retention near saturation (van den Elsen *et al.* 1999).

The application of this method is limited by the air-entry value of the porous plate and the length of the hanging water column. Suction tables, which use sand-silt packings as porous membranes, have been popular in the past to handle large numbers of core samples (Jamison, 1958). For pressures up to 20 bar (that is, where $h = -200$ m), the water-retention and unsaturated hydraulic-conductivity functions are determined using a pressure plate or a plate membrane apparatus.

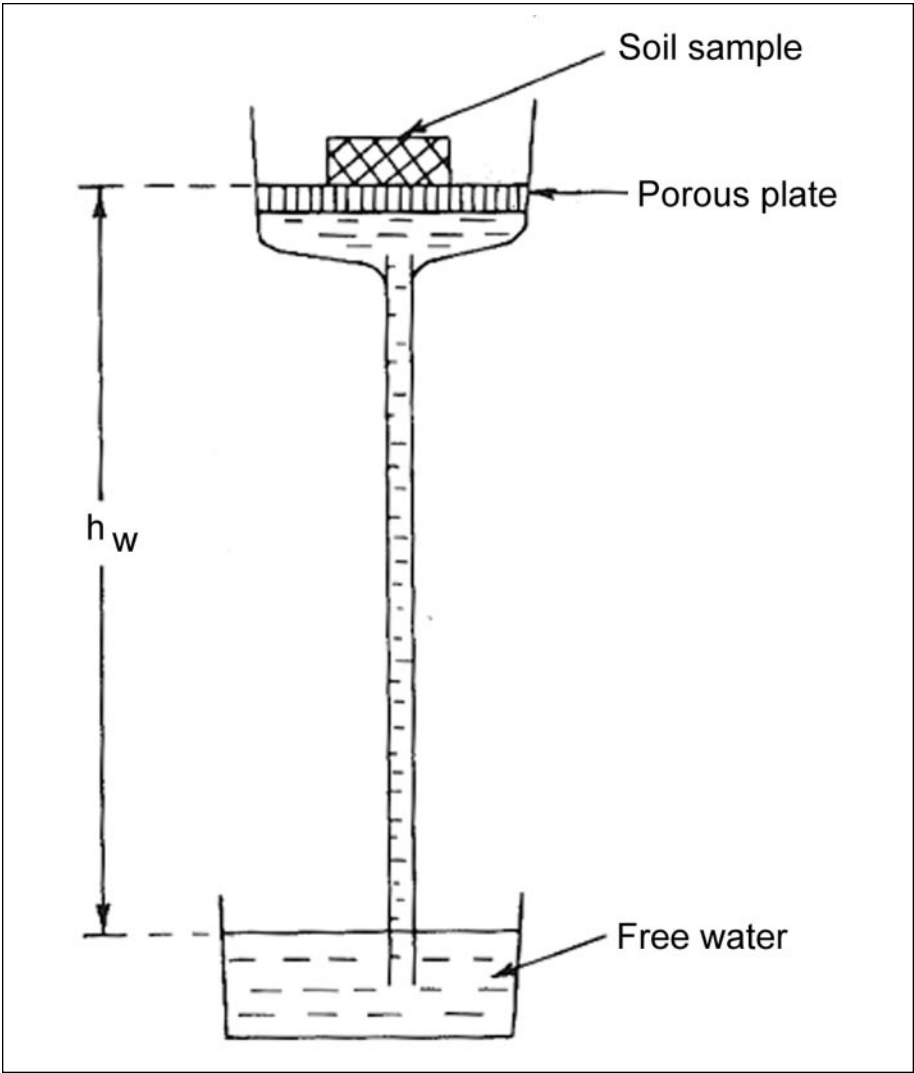


Figure 3-39. Tension plate assembly for determining the soil water retention by equilibrating a soil sample with a known matric suction value. This assembly is applicable for the range of matric suction of 0–0.8 bar (Hillel, 1981).

Figure 3-40 shows a generic setup of the pressure cell apparatus. Water is pushed out from the initially saturated sample by raising the gas-phase pressure in the cell above the plate while water and air below the plate are at atmospheric pressure. The soil sample is allowed to equilibrate for a sequence of air pressures used to obtain different soil matric pressures. The volume of water coming out of the soil sample as the pressure changes is used to calculate the changes in the soil saturation.

Different types of equipment and methods of changing the moisture content in a soil core are used, depending on the pressure range. For air pressures up to 1 bar (corresponding to $h = -100$ kPa), Tempe-pressure cells are frequently used. A soil core is held between two end caps, and air pressure is applied to the top cap while the bottom cap contains a ceramic plate attached to a burette measuring the outflow. The equili-

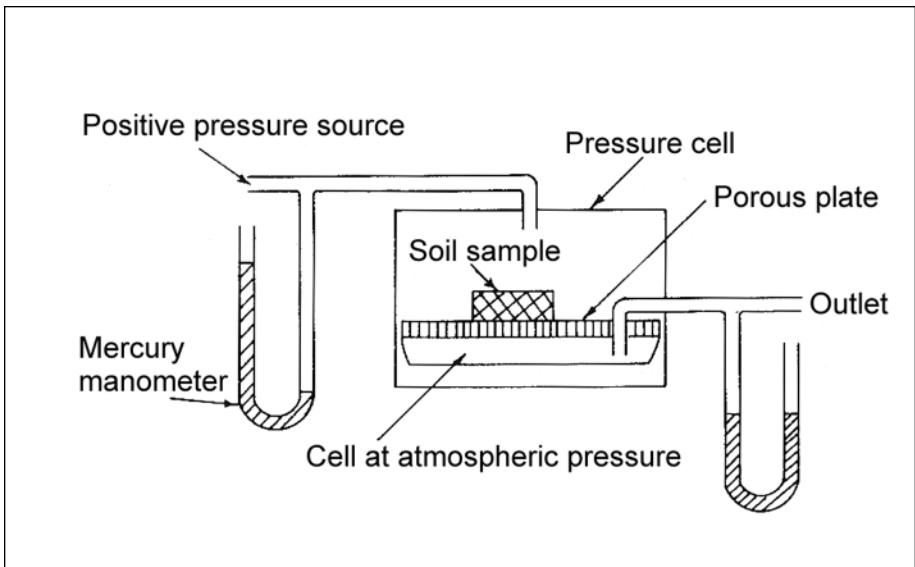


Figure 3-40. Pressure plate apparatus for determining the water retention in the high suction range using water extraction by applying positive air pressure above the soil sample. Note that the lower side of the porous plate is in contact with water at the atmospheric pressure (Hillel, 1981).

bration time depends on the plate bubbling pressure and the type of soils. The changes in the soil-water content are calculated from the outflow volume. If the outflow rate and the soil-water pressure head are monitored as a function of time, the unsaturated hydraulic conductivity function can be determined using inverse modeling (Eching *et al.* 1994). For higher pressures up to 20 bar (that is, $h = -2$ Mpa), several core samples or soil clods are placed on a ceramic plate in a pressure chamber. All equipment needed for this procedure is available commercially. In this case, the volumetric water content is obtained by weighing the samples. The bubbling pressure of the plate determines the range of pressures, typically 1 to 15 bar. Note that a disadvantage of the method is the long time to reach equilibrium.

Hydraulic Conductivity

The one-dimensional, head-controlled method flow experiments, has been the classical approach for steady-state determinations of the hydraulic conductivity (Klute and Dirksen 1986 and Dirksen 1991). The soil-water pressure head is controlled at both ends of the sample through a porous membrane, and tensiometers are installed in the vertical soil column to determine the hydraulic gradient needed to calculate the $K(h)$ function from Darcy's law. This method is effective for matric pressures of more than approximately -50 kPa. The disadvantage of the method is that the flux may vary over time because of changes in the porous-plate impedance and the plate-soil layer permeability of the plate-soil layer.

Figure 3-41 shows the experimental setup for the head-controlled method, which includes two porous plates to allow one to control the head at the top and bottom edges of the soil sample. Changes in soil-water content resulting from the pressure changes can be directly estimated from the outflow data. This setup can be used to determine both water-retention and hydraulic-conductivity functions using the steady and transient "one-step" and "multi-step" experiments. Using the one-step experiment, a vacuum of about -90 kPa is applied to drain water from the core, and the pressure is measured using a monitoring tensiometer installed in the core.

Multi-step flow experiments can be conducted using step-wise pressure changes in both the upper and lower porous plate. After the end of each transient step, the steady-state water-flow experiment is conducted.

The water-retention curve is determined from the outflow data during the transient regime of water flow. The unsaturated hydraulic-conductivity function is calculated from Darcy's law using the data on the steady-state flow rate and matric gradient in the core. Inverse modeling is used to analyze the transient flow data.

The flux-controlled method is an alternative for constant-head experiments. In this method, water is supplied at a prescribed rate to the soil column using porous plates connected to a controlled vacuum. Tensiometers are used to monitor the matric pressure in the soil core. Unit gradient conditions are established by adjusting flow rate or suction (van den Elsen 1999). The difficulty of this method lies in maintaining the uniform, steady-state water supply into the soil core, especially the very

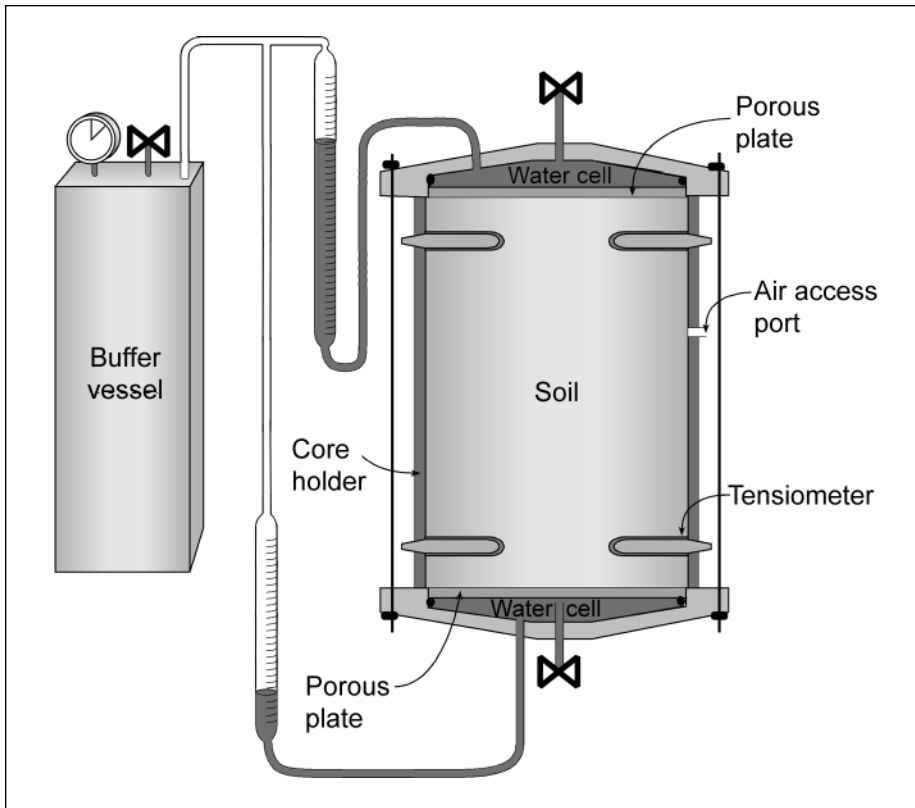


Figure 3-41. Principal scheme of core arrangement for soil drainage and saturation using axial flow experiments (Faybishenko, 1986)

small fluxes associated with lower conductivity values (cf. Dirksen 1999).

The evaporation method used by Wind (1969) constitutes a variation of the traditional flux-controlled method. An initially saturated soil sample is instrumented with tensiometers and placed on a balance. Water is allowed to evaporate from the top. The evaporation may be regulated by a fan. Hydraulic properties are determined in a similar manner for the instantaneous profile method. The method appears to have become more popular recently with the emergence of TDR, automated data collection and operation of equipment, and inverse modeling (cf. van Genuchten *et al.* 1999).

In a heterogeneous soil sample, the asymmetry of flow geometry with respect to the core axis and geometrical boundaries leads to a complex distribution of the moisture content and the flow field in the core (Finstlerle and Faybishenko 1999b). Two-dimensional inverse modeling should be used to analyze the results of laboratory experiments for such samples.

Radial-flow analysis has been used for quite some time to determine hydraulic properties. An experiment with radial-flow geometry was proposed by Richards *et al.* (1937) and was further developed by Richards and Richards (1951), Gardner (1960), and Klute *et al.* (1964). Richards and Richards (1962) and Klute *et al.* (1964) developed analytical solutions for radial-flow experiments. Klute *et al.* (1964) discussed the advantages of using radial-flow geometry rather than the more common axial-flow geometry. They noted that soil shrinkage during drying is significantly reduced in a design with a central porous cylinder, thus preventing loss of contact between the sample and the boundary. Furthermore, the air trapped in the porous cylinder can be removed easily and with minimal disturbance to the boundary. Because of the reduced flow distance for radial-flow geometry, a larger sample volume can be tested in a shorter time (Gardner 1960). Timlin and Pachepsky (1998) recently reported on the measurement of the conductivity function by optimizing the inflow and outflow to a ceramic-cup tensiometer that was subjected to various suctions.

Figure 3-42 shows a schematic of a flow cell apparatus for radial, single-step and multi-step desaturation experiments on soil samples. Faybishenko (1986) and Dzekunov *et al.* (1987) used this setup for

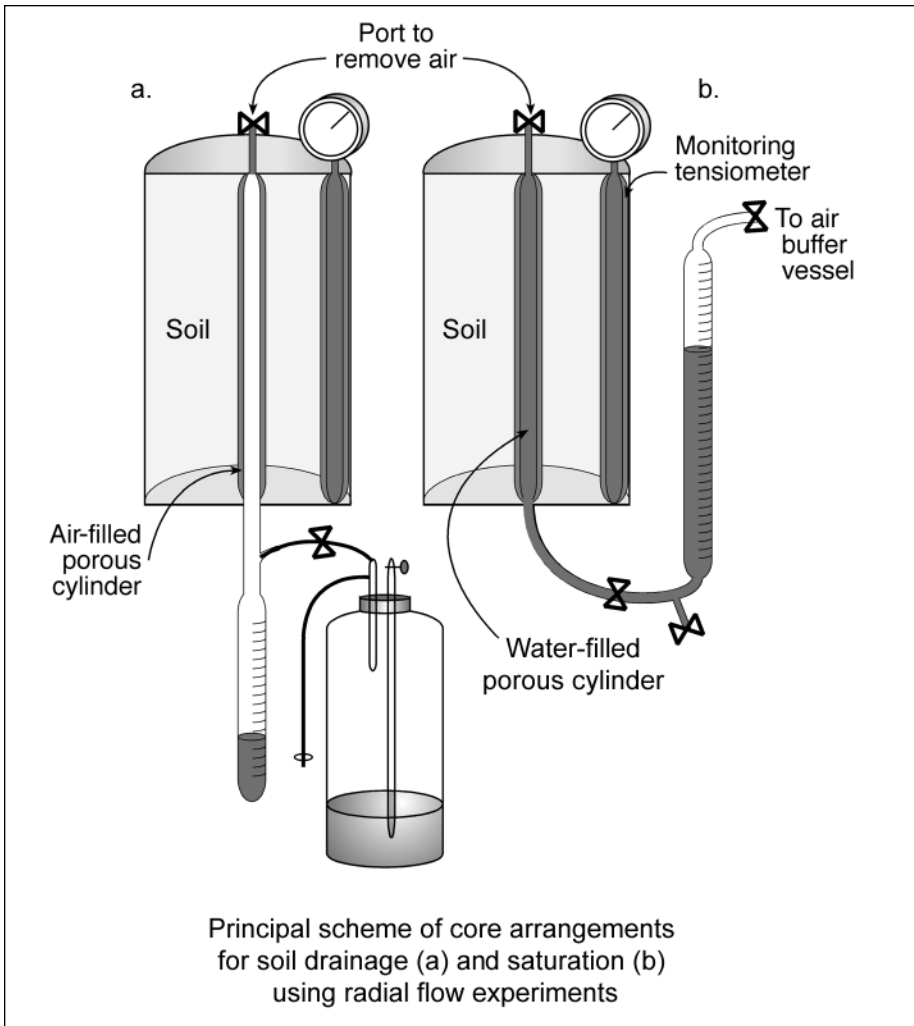


Figure 3-42. Principal scheme of core arrangements for soil drainage (a) and saturation (b) using radial flow experiments (Faybishenko, 1986)

radial-flow experiments with a central porous cylinder for both injection and extraction of water. A second porous cylinder was used as a monitoring tensiometer. Wetting and drying curves were obtained by applying one-step, multi-step, and continuously changing boundary pressures under isothermal and non-isothermal conditions. Soil cores (22 cm long

and 15 to 18 cm in diameter) were conserved in a solid metal or plastic cylinder, and the annulus was filled with a paraffin-tar mixture. A ceramic cylinder with an air-entry pressure of about 1 bar was inserted along the axis of the core in the center of the soil core. This cylinder was attached to a vacuum-regulated burette to measure the cumulative water discharge. The outlet is located at the bottom to facilitate free movement of the extracted water into the measuring burette to inhibit air accumulation in the cylinder (Elrick and Bowman 1964; Klute *et al.* 1964). A tensiometer was inserted near the outer wall of the flow cell. As confirmed by numerical simulations (Finsterle and Faybishenko 1999a), a one-dimensional, radial model can accurately describe flow.

Determining hydraulic properties in deforming porous media is a challenging but important and pertinent problem. Angulo-Jaramillo *et al.* (1999) presented an example of one-dimensional infiltration into a free-swelling, undisturbed sample of compacted clay. The laboratory setup is shown in Figure 3-43. Water flow processes in a deformable, porous medium can be monitored using a ^{241}Am and ^{137}Cs dual gamma-ray system and tensiometers connected to a differential-pressure transducer.

Globus and Gee (1995) used a temperature gradient to determine soil-water diffusivity and hydraulic conductivity for moderately dry soils. A partially wetted sample at uniform water content is sealed and equilibrated under an applied thermal gradient. When equilibrium is reached, liquid-phase flow from the cool end is equal to vapor-phase flow from the warm end. The nonuniform water profile in the core is then used to determine the unsaturated hydraulic-conductivity and water-retention functions. The water-content profile can be determined by sampling or, possibly, nondestructive methods. This method is time consuming but allows determination of very low unsaturated conductivities ranging from 10^{-7} to 10^{-12} cm/s. Furthermore, the conductivity represents the combined effects of vapor and liquid flow, which may be important for many practical applications.

Ultracentrifuge methods* have been used fairly recently to determine unsaturated hydraulic properties (Conca and Wright 1990, 1992, 1998;

*The section on ultracentrifuge methods was written by James L. Conca and Judith Wright.

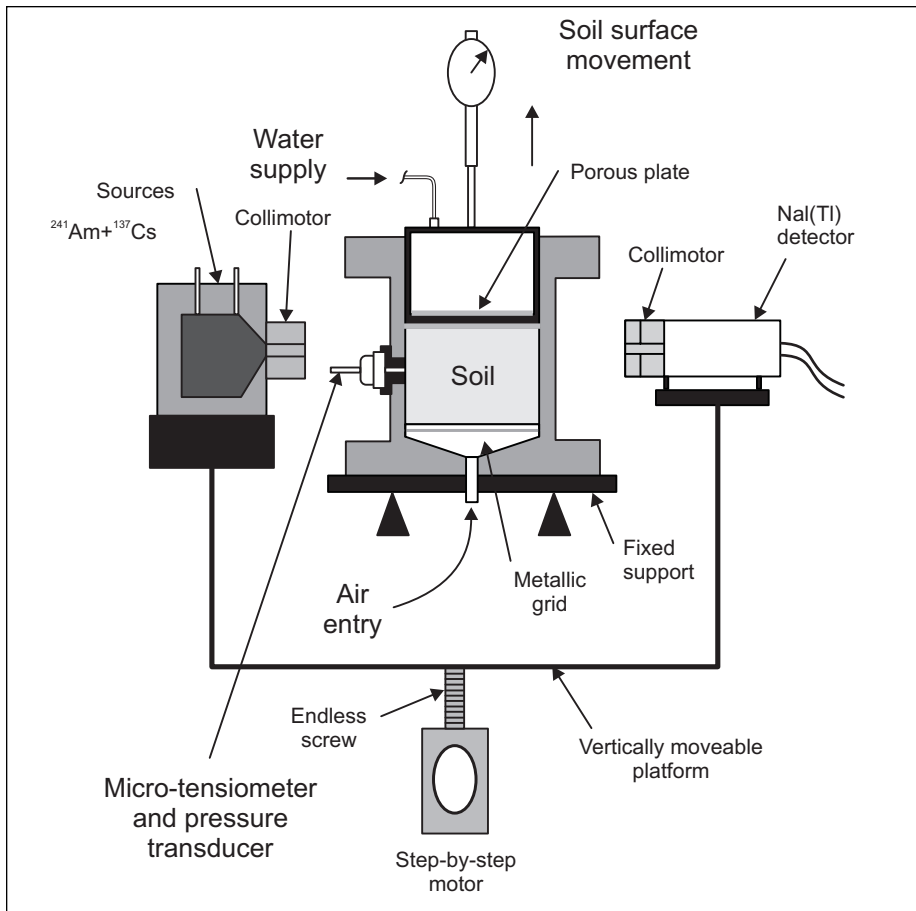


Figure 3-43. Rigid-wall permeameter for infiltration in unsaturated swelling soils with a dual-energy gamma-ray scanner system and micro-tensiometer (Angulo-Jaramillo *et al.* 1999)

Conca *et al.* 1999). In this method, a saturated soil sample is placed in a high-speed centrifuge and spun around. The sample desaturates during the centrifugation until a certain soil matric head is reached, which corresponds to a specified centrifugal speed. Water-retention points can be determined by weighing the sample. However, it is also possible to determine the conductivity by supplying water to the soil sample during the centrifugation (Nimmo 1990; Nimmo *et al.* 1987). After steady flow

conditions are established, the centrifugation is stopped and the sample is weighed to determine the water content. Retention and conductivity curves can be determined by repeating the process at increasingly higher speeds. Some disadvantages of the method are the limited sample size, compaction of finer-textured soils, and high equipment cost. The case study on the accompanying CD, "The UFA method for Characterization of Vadose Zone Behavior," by James L. Conca and Judith Wright, reports on the Unsaturated/Saturated Flow Apparatus (UFA) that determines hydraulic properties with the ultracentrifuge method. The device can be used to determine hydraulic conductivity, matric potential, electrical conductivity, vapor diffusivity, distribution coefficient, retardation factor, dispersivity, and thermal conductivity. The UFA instrument can achieve steady-state flow in hours using an ultracentrifuge with a constant, ultralow flow pump that provides fluid to the sample surface through a rotating seal assembly and microdispersal system. The ultracentrifuge can reach accelerations of up to 20,000 g (soils are generally run only to 1,000 g [3,000 rpm], an effective hydrostatic pressure of 2.5 bars). Constant flow rates can be reduced to 0.001 ml/h.

Multi-Liquid Systems

Hydraulic properties of porous media containing separate aqueous and nonaqueous liquid phases are of interest in petroleum and environmental engineering and remediation design. The pressure, saturation, and conductivity of two phases need to be considered. The consideration of parameters for two phases is in contrast with the hydraulic properties of air-water systems, where the air phase is usually of little interest and considered to be at atmospheric pressure. The terminology and methodology tends to vary somewhat for multi-fluid flow, but the principles are the same as for flow of water in an unsaturated soil (Dullien 1992; Corey 1994).

Retention

The retention curve, usually referred to as the capillary pressure–saturation curve, is frequently interpreted with the Laplace-Young equation for the pressure drop at the interface of a nonwetting and wetting fluid in a cylindrical tube:

$$P_c = P_n - P_w = \frac{2\sigma_{nw}}{r} \cos\phi_{snw} \quad (3.12)$$

where the subscripts n and w denote the nonwetting and wetting phases, ϕ_{snw} is the contact angle, σ is the tension at the air-water interface, r is the tube radius. In fractional or mixed wettability media, water and oil alternate as wetting fluids, depending on the saturation of the sample and the degree of hysteresis. The difference in oil and water pressure may therefore indicate a sign change (Bradford and Leij 1995). Lenhard and Parker (1988) measured the retention by controlling the saturation of the oil and water phases, rather than the pressures. Figure 3-44 shows a schematic of the experimental setup. The soil column contains hydrophobic and hydrophilic ring tensiometers, which are connected to fluid reservoirs to allow displacement of a known liquid volume into or from the column. The soil is allowed to equilibrate under atmospheric air pressure. The equilibrium liquid pressures are also determined with the tensiometers.

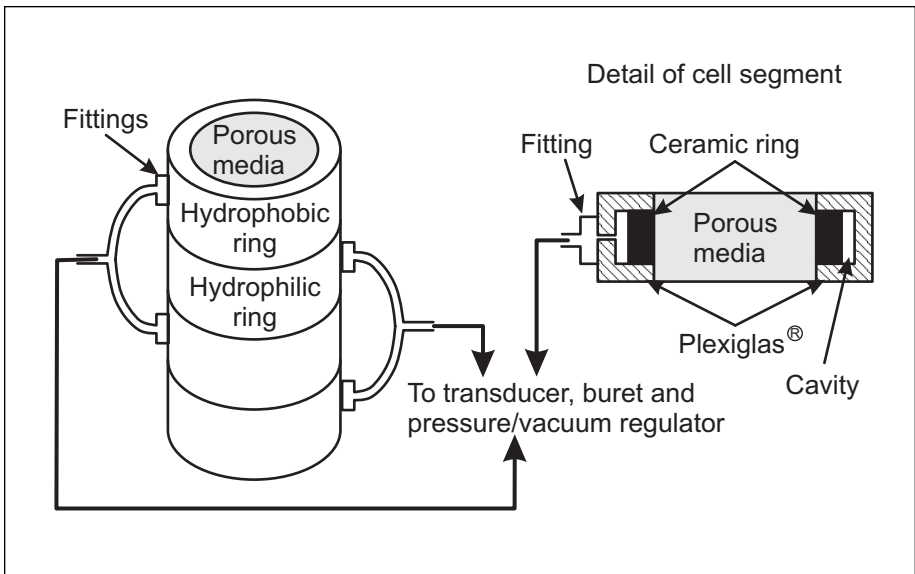


Figure 3-44. Schematic of an experimental apparatus consisting of hydrophilic and hydrophobic rings tensiometers for measuring retention in multi-liquid systems.

The experimental retention curve for a two-fluid system can be used to estimate the retention curve for a different pair of fluids in the same medium by the following scaling procedure:

$$P_{c2}(S) = \frac{\sigma_2 \cos \phi_2}{\sigma_1 \cos \phi_1} P_{c1}(S) \quad (3.13)$$

where the subscripts 1 and 2 denote a two-fluid system with known and unknown retention curves. Frequently identical contact angles are assumed, in which case the scaling is based on the ratio of interfacial tensions. Furthermore, the retention curves for a three-fluid system, schematically shown in Figure 3-45, can be estimated from the corresponding curves for two-fluid systems using Leverett's assumption. Additional procedures are needed to account for surface tensions and wettability (Bradford and Leij 1996).

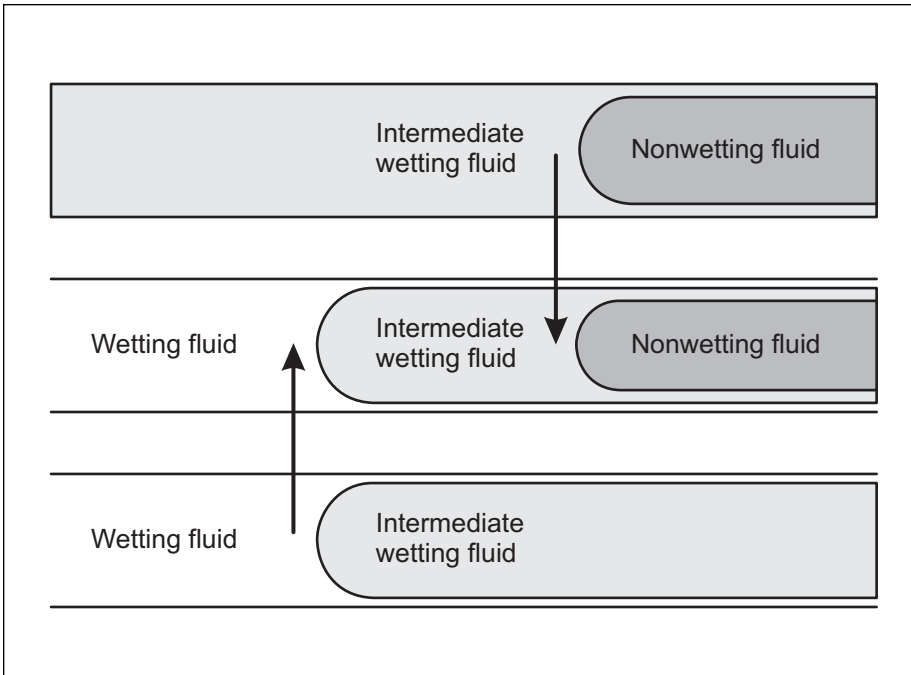


Figure 3-45. Schematic of the prediction of a three-fluid characteristic from two-fluid retention characteristic according to Leverett's principle.

Conductivity

The measurement of conductivities, usually referred to as relative permeability, is more cumbersome than the hydraulic conductivity for air-water systems, but the same principles of steady-state measurements are used (Demond and Roberts, 1993). A porous ceramic plate with Teflon inlays is placed on both sides of the soil core for separate application and collection of aqueous and nonaqueous liquids. Tensiometers are installed to determine liquid pressures. Ideally, the capillary pressure and liquid saturations should be constant throughout the sample. The approach can become quite time-consuming if the permeability needs to be characterized for three-fluid systems with mixed wettability (cf. Honarpour *et al.* 1986). Inverse modeling of transient flow processes can be used to determine hydraulic parameters for such multifluid systems.

INVERSE METHODS

The design of field and laboratory experiments is often restricted to simple steady-state boundary conditions because of limitations in the analytical methods used to determine the water unsaturated hydraulic functions. The determination of unsaturated hydraulic properties by inverse flow modeling has rapidly become popular as an alternative. Inverse solutions rely on numerical methods, which obviate most restrictive conditions and offer flexibility regarding the type of data that can be used, as well as the optimization and parameterization procedures employed to determine hydraulic parameters. Inverse modeling has been used to quantify hydraulic parameters of laboratory soil cores using one-step outflow (Toorman *et al.* 1992), multi-step outflow (Eching *et al.* 1994; Finsterle and Faybishenko 1999a), upward infiltration (Hudson *et al.* 1996), and evaporation (Simunek *et al.* 1998). Many applications to the field can be envisaged, such as the analysis of single- and multiple-disk infiltrometer data (Simunek and van Genuchten 1996, 1997; Zhang 1997). Specific implementation of inverse methods are summarized below and described in detail in Chapter 5.

A variety of optimization algorithms have been used to estimate several or all of the unknown hydraulic parameters from observed time-series data of the water flux, water content, and pressure head (Kool *et al.* 1987; Simunek and van Genuchten 1996; Abbaspour *et al.* 1997; Finsterle and Faybishenko 1999a). In the case of a multi-step outflow

experiment where a tensiometer is inserted in the soil (Eching *et al.* 1994), the parameter vector \mathbf{b} may be estimated by minimizing the following objective function (Hopmans and Simunek 1999):

$$O(\mathbf{b}) = W_Q \sum_{i=1}^N \{w_i [Q(t_i) - Q(t_i, \mathbf{b})]\}^2 + W_h \sum_{j=1}^M \{w_j [h(t_j) - h(t_j, \mathbf{b})]\}^2 + W_\theta \sum_{l=1}^L \{w_l [\theta(t_l) - \theta(t_l, \mathbf{b})]\}^2 \quad (3.14)$$

where N , M , and L refer to the number of observations that were made over time (t) of cumulative outflow, Q , matric head, h , and volumetric water content, θ , respectively, while the corresponding simulated variables also include the parameter vector \mathbf{b} as an independent variable. The objective function $O(\mathbf{b})$ is normalized with weighting factors W for different types of data; weighting of individual observation may be done with the factors w . The objective of this particular optimization procedure is to determine the parameter vector \mathbf{b} that minimizes $O(\mathbf{b})$. As mentioned above, independently measured hydraulic data may also be included in the objective function; this will extend the optimized hydraulic parameters beyond the range of the outflow experiment.

The hydraulic properties are often parameterized according to van Genuchten (1980) leading to, for example, the parameter vector $\mathbf{b} = \{\theta_r, \theta_s, \alpha, n, K_s, L\}$. Several other parametric models are given in the subsection "Analytic Functions," below.

Knowledge of the initial values and mathematical and physical constraints on the parameters in question may improve the performance of the optimization algorithm. Frequently, the inverse problem is ill-posed (Yeh 1986). The mathematical model may not be convex, leading to different estimates for the vector \mathbf{b} depending on the initial estimates. Furthermore, errors and uncertainty are associated with the physical model, observations, and parameterization. These errors can cause the vector \mathbf{b} to be unstable, especially for higher dimensions of the parameter vector. For many applications, it may not even be possible to determine a "true" parameter vector.

INDIRECT METHODS

Because field and laboratory experiments for determining unsaturated hydraulic properties of soils are still relatively time consuming and

expensive, and the results may not be accurate or reproducible (especially for heterogeneous soils), indirect methods of estimating the parameters can be used. Indirect methods encompass a wide array of procedures developed to estimate hydraulic properties with “surrogate” data that are easily measured and, hence, commonly available (for example, particle-size distribution, bulk density, organic carbon content, and porosity). The process of predicting *needed* soil data from *existing* soil data is known as the pedotransfer function approach and is based on empirical and quasi-empirical functions and algorithms that establish the relationships between surrogate input data and unsaturated hydraulic-parameter output data.

Analytical Functions

Analytical expressions to describe hydraulic properties are convenient for characterizing soils and for use in numerical models (van Genuchten *et al.* 1991; Marion *et al.* 1994). Many closed-form expressions have been proposed to describe hydraulic properties. A limited number of papers were published to evaluate their suitability (Alexander and Skaggs 1986; Globus 1987; Mualem 1976; van Genuchten and Nielsen 1985; Vereecken 1992; Leij *et al.* 1997). A case study on the accompanying CD, “Closed Form Expressions for Water Retention and Conductivity Data,” by F.J. Leij, W.B. Russell, and S.M. Lesch, compares 14 water-retention and 11 unsaturated-conductivity functions. A few selected functions describing the hydraulic data fairly well are briefly presented below (see also Leij *et al.* 1997).

The Brooks-Corey water-retention function (Brooks and Corey, 1964) has long been used to describe water-retention data for relatively homogeneous soils with a narrow pore-size distribution:

$$S_e(h) = \frac{\theta - \theta_r}{\theta_s - \theta_r} = \begin{cases} 1 & \alpha h \leq 1 \\ (\alpha h)^\lambda & \alpha h > 1 \end{cases} \quad (3.15)$$

where S_e is the effective saturation, θ is the volumetric water content, and the subscripts r and s denote residual and saturated water contents. A disadvantage of the expression is the abrupt change of the $S_e(h)$ curve at $h = 1/\alpha$, denoting the pressure at which the largest pore drains.

The van Genuchten water-retention closed-form expression, which appears to be the most widely used since publication of the paper by van Genuchten (1980), is given by

$$S_e(h) = [1 + (\alpha h)^n]^{-m} \quad (3.16)$$

Frequently, the restriction $m \equiv 1-1/n$ is imposed in a pore-size distribution model to predict the unsaturated hydraulic conductivity.

Hutson and Cass (1987) proposed a two-part expression, including a parabolic equation close to saturation and a power function elsewhere:

$$S_e(h) = \begin{cases} 1 - (\alpha h)^2 S_i^{2/n} (1 - S_i) & h \leq h_i \\ (\alpha h)^{-n} & h > h_i \end{cases} \quad (3.17)$$

where $h_i = 1/(\alpha S_i^{1/n})$ and $S_i = 2/(2 + n)$

This expression ensures continuity in both $S_e(h)$ and $dS_e(h)/dh$ at $h = h_i$, unlike the Brooks-Corey function.

The following unsaturated hydraulic conductivity function, similar to the one used by Gardner (1958), can be used to describe $K(h)$ data:

$$K(h) = K_s [1 + (\alpha h)^n]^{-m} \quad (3.18)$$

where K_s is the saturated hydraulic conductivity.

The Brooks-Corey and van Genuchten water-retention functions were used to derive unsaturated hydraulic-conductivity functions given, correspondingly, by

$$K(S_e) = K_s S_e^{3+2/L} \quad (3.19)$$

$$K(S_e) = K_s S_e^L [1 - (1 - S_e^{1/m})^m]^2 \quad (3.20)$$

K_s is the saturated hydraulic conductivity (cm day^{-1}), and L is a lumped parameter that accounts for pore tortuosity and connectivity, and it is often assumed $L = 0.5$. Equation (3.20) is often called the Mualem-van Genuchten model, and the parameter m is given by $m = 1-1/n$; sometimes it is assumed that $L=0.5$.

Empirical Models of Pedotransfer Functions

Definition of Pedotransfer Functions

Empirical pedotransfer functions (PTFs) are used to determine soil hydraulic properties from soil texture and other readily available soil physical properties without relying on specific analytical models. The relationship between input and output parameters of a PTF is determined by a statistical-regression or neural-network analysis. These methods determine empirical coefficients for analytical functions by minimizing the difference between the predicted and observed results. Note that empirically determined parameters are mostly reliable only for conditions identical to those for which the PTFs were determined.

Whereas many PTFs exist for determining water-retention functions, only a few exist for saturated hydraulic conductivity, K_s , and unsaturated hydraulic conductivity. Initially, PTFs were used to determine specific points of the water-retention curves, such as the field capacity and wilting points (Jamison and Kroth 1958). Currently, PTFs are almost exclusively used to predict unsaturated hydraulic parameters, which are then used in numerical modeling.

Almost all PTFs rely on particle-size distribution data. With only a soil textural classification, simple “class” PTFs can be used to assess average hydraulic properties for each soil textural class (Carsel and Parrish 1988; Wösten *et al.* 1995). For a given particle-size distribution, a continuous PTF can be determined with textural percentages as independent variables. PTF predictions may be further improved by adding basic soil properties such as bulk density, porosity, or organic matter content (Rawls and Brakensiek 1985; Vereecken *et al.* 1989; Rawls *et al.* 1991). Additional improvements may be achieved by including one or more water-retention data points (Rawls *et al.* 1992; Williams *et al.* 1992). Ahuja *et al.* (1989) and Messing (1989) improved predictions of the saturated hydraulic conductivity, K_s , by using effective porosity data, which they defined as the total porosity minus the water content at -10 or -33 kPa pressure head.

The reliability and accuracy of PTFs are important issues since most PTFs are developed by sparse, noisy, and sometimes ambiguous data sets that may yield parameter estimates with large confidence intervals. The accuracy of PTFs should be assessed against independent data sets

as it was done by Tietje and Tapkenhinrichs (1993), Kern (1995), and Tietje and Hennings (1996).

Regression Analysis

Brakensiek *et al.* (1984) and Rawls and Brakensiek (1985) presented PTFs that predict parameters from the Brooks-Corey equation (3.16) and saturated hydraulic conductivity, K_s as well as from porosity, ϕ , and sand and clay percentages (S and C , respectively). In these approaches, θ_s is set equal to the porosity while θ_r , $h_b = 1/\alpha$, λ , and K_s are related to S , C , and ϕ , employing a regression equation given by:

$$b_i = a_1 + a_2S + a_3C + a_4\phi + a_5S^2 + a_6C^2 + a_7\phi^2 + a_8S\phi + a_9C\phi + a_{10}S^2C + a_{11}S^2\phi + a_{12}C^2\phi + a_{13}SC^2 + a_{14}C\phi^2 + a_{15}S^2\phi^2 + a_{16}C^2\phi^2 \quad (3.21)$$

where b_i is a component of the hydraulic parameter vector $\mathbf{b} = \{\theta_r, h_b, \lambda, K_s\}$, and a_i are the input coefficients. This model is applicable for sand percentages between 5% and 70% and clay percentages between 5% and 60% (Rawls *et al.* 1991, 1992). The coefficients a_i are summarized in Table 3-17.

Vereecken *et al.* (1989, 1990) provided expressions for water retention and unsaturated hydraulic conductivity for 182 Belgian soil horizons. The water retention was described by modifying equation (3.16) and setting $m = 1$. The unsaturated hydraulic conductivity was described according to Gardner (1958) (see also equation 3.18):

$$K(h) = \frac{K_s}{1 + (bh)^c} \quad (3.22)$$

where b and c are empirical parameters.

According to Vereecken *et al.* (1989, 1990), the expressions for θ_r , θ_s , α (1/cm), n , K_s (cm/day), b , and c are:

$$\begin{aligned} \theta_r &= 0.015 - 0.005C + 0.014OM \\ \theta_s &= 0.81 - 0.238BD + 0.014OM \\ \ln(\alpha) &= -2.486 + 0.025S - 0.023C - 2.617BD - .0351OM \\ \ln(n) &= 0.053 - 0.009S - 0.013C + 0.00015S^2 \\ \ln(K_s) &= 20.62 - 0.96 \ln(C) - 0.66 \ln(S) - 0.46 \ln(OM) - 8.43BD \\ \ln(b) &= -0.73 - 0.01877S + 0.058C \\ \ln(c) &= -1.186 - 0.194 \ln(C) - 0.0489 \ln(Si) \end{aligned} \quad (3.23)$$

TABLE 3-17

Coefficients of the PTFs Determined by Brakensiek et al. (1984) and Rawls and Brakensiek (1985) for Prediction of Brooks-Corey Parameters and K_s .

Index a_i	Variables	Input Coefficients			
		θ_r , cm ³ /cm ³	$\ln(h_b)$, cm	$\ln(\lambda)$	$\ln(K_s)$, cm/h
1	Intercept	-0.01825	5.339674	-0.78428	-8.96847
2	S	0.000873	0	0.017754	0
3	C	0.005135	0.184504	0	-0.02821
4	ϕ	0.029393	-2.48395	-1.0625	19.52348
5	S^2	0	0	-5.3E-05	0.000181
6	C^2	-0.00015	-0.00214	-0.00273	-0.00941
7	ϕ^2	0	0	1.111349	-8.39522
8	$S\phi$	-0.00108	-0.04356	-0.03088	0.077718
9	$C\phi$	0	-0.61745	0	0
10	S^2C	0	-1.3E-05	-2.4E-06	1.73E-05
11	$S^2\phi$	0	-0.00072	0	0.001434
12	$C^2\phi$	0.000307	0.008954	0.007987	0.02733
13	SC^2	0	5.4E-06	0	-3.5E-06
14	$C\phi^2$	-0.00236	0.500281	-0.00674	0
15	$S^2\phi^2$	0	0.001436	0.000266	-0.00298
16	$C^2\phi^2$	-0.00018	-0.00855	-0.00611	-0.01949

where S , C , and Si are the percentages of sand, clay, and silt; BD signifies the bulk density (g/cm³); and OM stands for the organic matter percentage.

Neural-Network Analysis

Artificial neural networks (ANNs) have been used to estimate hydraulic parameters by Pachepsky *et al.* (1996), Schaap and Bouten (1996), and Tamari *et al.* (1996). Neural networks are sometimes described as “universal function approximators” because of their ability to “learn” how to approximate a continuous (nonlinear) function to a desired degree of accuracy (Hecht-Nielsen, 1990; Haykin, 1994). An advantage of PTFs derived with a neural-network method is that no *a priori* model is required. Instead, the optimal relations between input

data (basic soil properties) and output data (hydraulic parameters) are determined during the analysis with an iterative calibration procedure. The relationship is established with weighting factors for nodes at input, hidden, and output layers of the network. The number of input and output nodes corresponds to the number of input and output variables of the PTF (Schaap and Bouten 1996).

Although artificial neural networks may yield more accurate PTFs than a regression analysis (Schaap *et al.* 1998, Tamari 1996), their disadvantages are that (1) except for trivially small networks, it is cumbersome to formulate explicit expressions for the PTF, (2) the network may be too complex, and (3) the calibration involves too many iterations (Schaap *et al.* 1999).

Water-Retention Function and Saturated Hydraulic Conductivity

With a database of 1,209 samples, Schaap *et al.* (1998) determined neural-network PTFs with the retention parameters given by equation (3.16), and with $m = 1-1/n$ and the saturated hydraulic conductivity, K_s . Schaap *et al.* used a feed-forward back-propagation method with input, hidden, and output layers calibrated with the bootstrap method (Efron and Tibshirani 1993). Schaap *et al.* (1998) calibrated neural-network models to predict retention parameters and K_s with five different data sets and then recalibrated the models for an enlarged database of 2,085 samples. A summary of these models is given in Table 3-18, which presents parameters based on measured data (unlike a similar PTF by Carsel and Parrish 1988, which is based on predictions made by another PTF developed by Rawls and Brakensiek 1985). In Table 3-18, Model 1 (TXT) uses the average of “observed” hydraulic parameters within textural classes of the USDA-SCS soil classification. Models 2 through 5 use progressively more detailed input data. Model 2 uses the sand, silt, and clay fractions (SSC). Model 3 additionally uses a bulk density value (BD). Models 4 and 5 also require one or two water-retention points (moisture content) at 33 and 1500 kPa suction (TH33 and TH1500). These particular points are routinely available in the large USDA/NRCS NSSC database (Soil Survey Staff 1995). It is evident from Table 3-18 that R^2 (coefficient of determination) increases and RMSE (the root mean square for error) decreases with respect to “observed” parameters when the number of input variables increases, which indicates that the accuracy of the water-retention-function calculations increases.

TABLE 3-18**Coefficients of Correlation and RMSE between Observed and Predicted Water Retention Parameters and Saturated Hydraulic Conductivity**

Model No.	Input data	Water retention parameters					Saturated Hydraulic Conductivity	
		R ²				RMSE	R ²	RMSE
		θ_r	θ_s	α	n	cm ³ /cm ³		Log (cm/day)
1	TXT	0.066	0.136	0.204	0.452	0.108	0.425	0.741
2	SSC	0.073	0.150	0.221	0.472	0.107	0.437	0.735
3	SSCBD	0.070	0.567	0.232	0.479	0.093	0.509	0.685
4	SSCBDTH33	0.090	0.589	0.380	0.569	0.066	0.609	0.611
5	SSCBDTH331500	0.339	0.585	0.550	0.743	0.063	0.613	0.610

Unsaturated Hydraulic Conductivity

Adopting similar techniques, Schaap and Leij (2000) developed neural-network PTFs to estimate parameters of the Mualem-van Genuchten model (equation 3.20). With a database of 235 soils, Schaap and Leij (2000) determined that from water-retention parameters θ_r , θ_s , α , and n , the unsaturated hydraulic conductivity can be predicted with an accuracy of 0.84 log(cm/day), that is, within one order of magnitude. Similar results were reported by Kosugi (1999) for a different water-retention function.

It is important to assess the uncertainty involved in determining unsaturated hydraulic parameters. The neural-network calibration with the bootstrap method made it possible to quantify the uncertainty associated with the PTF prediction for a given sample. Figure 2 of the case study “Estimation of Soil Hydraulic Properties” by Schaap *et al.* shows the water-retention and unsaturated hydraulic-conductivity curves with the 10% and 90% confidence intervals as predicted by Model 3 (Table 3-18) for a loamy sand and a clay sample. The entire probability distribution is given for the saturated hydraulic conductivity, K_s . The uncertainty in the predicted hydraulic properties for clay is higher than that for loamy sand. Note that the neural-network calibration for fine-

textured soils was conducted with a relatively small number soil samples, and hence the PTF cannot predict hydraulic properties of the clay as accurately as for sand. The case study “Estimation of the Soil Hydraulic Properties”, by Marcel G. Schaap, Feike J. Leij, and Martinus Th. Van Genuchten, U.S. Salinity Laboratory, USDA-ARS, describes several indirect methods of determining soil hydraulic properties, including neural network analysis (see page 500).

The five PTF models were implemented in a user-friendly Windows 95 program called Rosetta, which specifies input data to predict the hydraulic parameters θ_r , θ_s , α , n , K_s , K_0 and L of equations (3.16) and (3.23), where K_0 is used as matching point for the saturated conductivity in model (3.23) rather than the experimental value for K_s . The program also quantifies the standard deviation of the estimated parameters. Hydraulic parameters can then be used in simulation models while uncertainty estimates facilitate risk-based analyses of water and solute transport. Rosetta is available for download at <http://www.ussl.ars.usda.gov/MODELS/rosetta/rosetta.HTM>.

Finally, Table 3-19 includes the water-retention parameters θ_r , θ_s , α , n , and the saturated hydraulic-conductivity parameter, K_s , and the unsaturated conductivity parameters K_s , and L , obtained by textural averages (Model 1 in Table 3-18).

Methods Based on Particle-Size and Pore-Size Distributions

Particle-Size Distribution

For various textured soils, a remarkable similarity between cumulative particle-size distribution curves and water-retention curves was observed (Arya and Paris 1981; Haverkamp and Parlange 1986). The particle-size distribution (PSD) can determine a pore-size distribution function, which can then be used to estimate water-retention and unsaturated hydraulic-conductivity functions (Arya and Paris 1981; Arya *et al.* 1999a; Arya *et al.* 1999b; Hoffmann-Riem *et al.* 1999). This method by Arya is based on the hypothesis that the discrete soil particle domains are assembled together without mixing of various-size particles. The resulting assemblage has the same water-retention curves and unsaturated hydraulic-conductivity functions as its counterpart natural soil, in which natural particles are mixed.

TABLE 3-19**Average Values of the Unsaturated Hydraulic Parameters for the Twelve USDA Textural Classes.**

Standard deviations are given in parentheses.

Texture Class	N	θ_r cm ³ /cm ³	θ_s cm ³ /cm ³	Log(α) log(1/cm)	log(n)	K_s log(cm/day)	K_o log (cm/day)	L
Clay	84	0.098 (0.107)	0.459 (0.079)	-1.825 (0.68)	0.098 (0.07)	1.169 (0.92)	0.472 (0.26)	-1.561 (1.39)
C loam	140	0.079 (0.076)	0.442 (0.079)	-1.801 (0.69)	0.151 (0.12)	0.913 (1.09)	0.699 (0.23)	-0.763 (0.90)
Loam	242	0.061 (0.073)	0.399 (0.098)	-1.954 (0.73)	0.168 (0.13)	1.081 (0.92)	0.568 (0.21)	-0.371 (0.84)
L Sand	201	0.049 (0.042)	0.390 (0.070)	-1.459 (0.47)	0.242 (0.16)	2.022 (0.64)	1.386 (0.24)	-0.874 (0.59)
Sand	308	0.053 (0.029)	0.375 (0.055)	-1.453 (0.25)	0.502 (0.18)	2.808 (0.59)	1.389 (0.24)	-0.930 (0.49)
S Clay	11	0.117 (0.114)	0.385 (0.046)	-1.476 (0.57)	0.082 (0.06)	1.055 (0.89)	0.637 (0.34)	-3.665 (1.80)
S C L	87	0.063 (0.078)	0.384 (0.061)	-1.676 (0.71)	0.124 (0.12)	1.120 (0.85)	0.841 (0.24)	-1.280 (0.99)
S loam	476	0.039 (0.054)	0.387 (0.085)	-1.574 (0.56)	0.161 (0.11)	1.583 (0.66)	1.190 (0.21)	-0.861 (0.73)
Silt	6	0.050 (0.041)	0.489 (0.078)	-2.182 (0.30)	0.225 (0.13)	1.641 (0.27)	0.524 (0.32)	0.624 (1.57)
Si Clay	28	0.111 (0.119)	0.481 (0.080)	-1.790 (0.64)	0.121 (0.10)	0.983 (0.57)	0.501 (0.27)	-1.287 (1.23)
Si C L	172	0.090 (0.082)	0.482 (0.086)	-2.076 (0.59)	0.182 (0.13)	1.046 (0.76)	0.349 (0.26)	-0.156 (1.23)
Si Loam	330	0.065 (0.073)	0.439 (0.093)	-2.296 (0.57)	0.221 (0.14)	1.261 (0.74)	0.243 (0.26)	0.365 (1.42)

The pore-size distribution is estimated from the total soil-sample pore volume, which may be determined from particle and bulk density data, and particle-size distribution (PSD). The relationship between particle and pore radii is well defined for spherical particles arranged in a cubic, close-packed assemblage, but requires empirical corrections for natural-soil particles. By calculating pore radii, pressure heads are subsequently calculated. This conversion necessitates additional empirical corrections to account for water not held by capillary forces and unknown effects of fluid and solid properties on water retention.

Pore-Size Distribution

Analytical models for the conductivity function can be derived by representing the porous medium as an idealized medium, consisting of well-defined pores with a uniform pore-size or a known pore-size distribution. Usually, pore and solid geometry are simplified considerably. Since the pore system of real porous media is not as simple as these models assume, empirical parameters are included in the models to improve the fit between experimental and theoretical conductivity functions.

Two of the most popular pore-size distribution models for conductivity are those by Burdine (1953):

$$K (S_e) = K_s S_e^L [\int_0^{S_e} h^{-2}(x) dx / \int_0^1 h^{-2}(x) dx] \quad (3.24)$$

and Mualem (1976):

$$K (S_e) = K_s S_e^L [\int_0^{S_e} h^{-1}(x) dx / \int_0^1 h^{-1}(x) dx]^2 \quad (3.25)$$

where, as before, K_s is the saturated hydraulic conductivity, L is a pore-connectivity and tortuosity parameter, and x is a dummy integration variable.

Databases

Soil hydraulic databases can provide surrogate information when the direct measurement of soil hydraulic properties is not feasible because of cost, time, and uncertainty (Schaap and Leij 1998). Several collections of soil hydraulic data have been compiled (Mualem 1976; Rawls *et al.* 1985; Wösten and van Genuchten 1988; Leij *et al.* 1996; Lilly *et al.* 1999). The International Unsaturated Soil Hydraulic Database

(UNSODA) (Leij *et al.* 1996) contains data sets from around the world for a variety of porous media (see also the case study on the accompanying CD “The UNSODA Unsaturated Soil Hydraulic Database,” by F.J. Leij, W.J. Alves, M. Th. van Genuchten, A. Nemes, and M.G. Schaap). The UNSODA database currently consists of 791 entries of field- and laboratory-measured water-retention, saturated and unsaturated hydraulic-conductivity, and particle-size-distribution data and bulk density from many international sources. Leij *et al.* (1996) documents UNSODA 1, intended for computers with a Disk Operating System (DOS). The database UNSODA 2 was developed for computers with the Windows 95 operating system using Microsoft Access. UNSODA 2 facilitates broad and user-friendly search and report procedures whereas UNSODA 1 has data entry and optimization routines. UNSODA 2 and supporting documentation may be obtained electronically (<http://www.usssl.ars.usda.gov>).

Several other databases of soil information and hydraulic data exist. The Natural Resources Conservation Service Soil Survey Laboratory in Lincoln, Nebraska, has compiled a database with soil characterization and profile description data. This database is distributed on a CD-ROM (<http://www.statlab.iastate.edu/soils/ssl/cdinfo.html>). Many other sites contain useful general information, such as those for Canadian (<http://res.agr.ca/CANSIS/NSDB/>) and Australian (<http://www.cbr.clw.csiro.au/aclep>) soils. The FAO and the International Soil Reference and Information Centre have compiled information for soils worldwide (FAO 1993, 1995). The Hydraulic Properties of European Soils (HYPRES) database will be maintained by the European Soil Bureau (Lilly *et al.* 1999). The Grizzly database contains hydraulic properties as well as structural and textural information on soils from different countries. Free copies of the database may be obtained electronically (<ftp://lthe712c.hmg.inpg.fr/pub/Grizzly>). Finally, commercial software is also available to estimate soil mechanical and hydraulic properties (<http://www.soilvision.com/home.html>).

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